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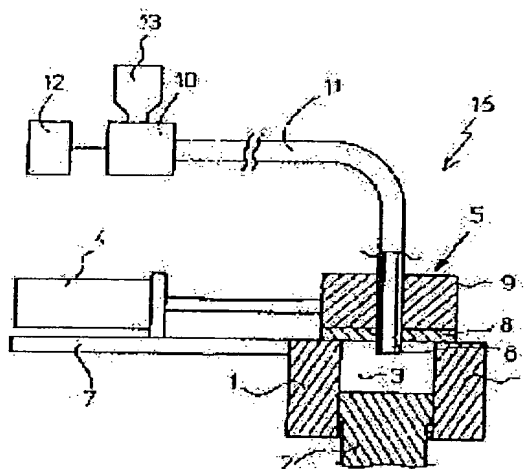
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(54) MANUFACTURING METHOD OF RARE EARTH SINTERED MAGNET AND RING MAGNET

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a high-performance rare earth sintered magnet that has a small content of oxygen, high density, and an improved degree of orientation, as compared with the conventional one.

SOLUTION: In this manufacturing method of rare earth sintered magnets, alloy coarse powder for the rare earth sintered magnet is ground minutely to an average particle diameter of 1 to 10 μm in a non-oxidizing atmosphere, and the obtained fine particle is collected into the non-oxidizing liquid for manufacturing slurry. In this case, the non-oxidizing liquid includes at least one kind of oil selected from mineral, synthetic, and vegetable oils, and lubricant comprising at least one kind selected from the monohydric alcohol ester of fatty acid, the monohydric alcohol ester of polybasic acid, the fatty acid ester of polyhydric alcohol, and their derivatives. Then, the formation is made by the slurry, and the forming body obtained is subjected to deoiling, sintered, and then heat-treated.



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CLAIMS

[Claim(s)]

[Claim 1] At least one sort of oils which pulverize the alloy coarse powder for rare earth sintered magnets in mean particle diameter of 1-10 micrometers in a non-oxidizing atmosphere, and are chosen from mineral oil, synthetic oil, and vegetable oil in the obtained fines, Collect in the non-oxidizing quality liquid which consists of lubricant which consists of at least one sort chosen from among the monohydric alcohol ester of a fatty acid, the monohydric alcohol ester of polybasic acid, the fatty acid ester of polyhydric alcohol, and those derivatives, and a slurry is produced. Subsequently, the manufacture approach of the rare earth sintered magnet characterized by fabricating by said slurry, deoiling the acquired Plastic solid, sintering subsequently, and heat-treating.

[Claim 2] The addition of said lubricant is the manufacture approach of the rare earth sintered magnet according to claim 1 which is the range used as the (R-Fe-B system alloy fines) (lubricant) =99.99-99.5 weight section:0.01 - 0.5 weight section.

[Claim 3] Said alloy coarse powder for rare earth sintered magnets is R (R is at least one sort of the rare earth elements containing Y). Nd occupied to R is more than 50 atom % -- :28-33%, B:0.8 - 1.5%, Co:0.5-5%, and Cu: -- 0.01 to 0.3% Ga: 0.01-0.2%, aluminum:0.01-0.3%, Nb:0.01-0.8%, and the remainder: The major component of Fe, and the manufacture approach of the rare earth sintered magnet according to claim 1 or 2 which consists of an unescapable impurity.

[Claim 4] By weight %, R (R is at least one sort of rare earth elements containing Y, and Nd occupied to R is more than 50 atom %):28 - 33%, B:0.8 - 1.5%, Co:0.5-5%, Cu:0.01-0.3%, And the remainder : It is the ring magnet which consists of a major component of Fe, and a R-Fe-Co-Cu-B system sintered magnet containing an unescapable impurity. The amount of oxygen contained unescapable to the total weight of said ring magnet is 0.3% or less. It has polar anisotropy and a consistency is more than 7.56 Mg/m³ (g/cm³). X diffraction peak intensity [from the field (105) observed in the magnetic pole period core surface location in a ring outer-diameter side]: -- I (105) and X diffraction peak intensity [from a field (006)]: -- the ring magnet with which a ratio with I (006) is characterized by being I(105)/I(006) =0.5-0.8.

[Claim 5] Said ring magnet is a ring magnet according to claim 4 which is weight % and contains Ga:0.01-0.2%, aluminum:0.01-0.3%, and Nb:0.01-0.8%.

[Claim 6] By weight %, the major component of R (R is at least one sort of rare earth elements containing Y, and Nd occupied to R is more than 50 atom %):28 - 33%, B:0.8 - 1.5%, Co:0.5-5%, Cu:0.01-0.3%, and remainder:Fe, And it is the ring magnet which consists of a R-Fe-Co-Cu-B

system sintered magnet containing an unescapable impurity. The amount of oxygen contained unescapable to the total weight of said ring magnet is 0.3% or less. It has an parallel anisotropy and a consistency is more than 7.56 Mg/m³ (g/cm³). The coercive force iH_c of a room temperature is more than 1.1 MA/m (14kOe). The amount of preferred orientation which the residual magnetic flux density ($Br//$) of the direction of orientation in a room temperature and the residual magnetic flux density (Br^{**}) of the die-length direction perpendicular to the direction of orientation define : $[(Br//) / (Br// + Br^{**}) \times 100(\%)]$ Ring magnet characterized by being 85.5% or more.

[Claim 7] Said ring magnet is a ring magnet given in the claim 6 which is weight % and contains Ga:0.01–0.2%, aluminum:0.01–0.3%, and Nb:0.01–0.8%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is a hypoxia content, has a high sintered compact consistency and relates to the manufacture approach which can obtain the rare earth sintered magnet of the high performance which raised the amount of preferred orientation compared with the former. Moreover, this invention is a hypoxia content, has a high sintered compact consistency and relates to the R-T-B system sintered ring magnet of high performance which raised the amount of preferred orientation of the polar-anisotropic direction or an parallel anisotropy compared with the former.

[0002]

[Description of the Prior Art] A R-Fe-B system sintered magnet (R is at least one sort of the rare earth elements containing Y) carries out coarse grinding of the R-Fe-B system alloy of a predetermined presentation, and is manufactured by pulverizing, fabricating impalpable powder with a mean particle diameter of 1–10 micrometers obtained among a magnetic field, sintering it subsequently, and subsequently, heat-treating it in the inert gas of N₂ grade. A residual magnetic flux density Br and maximum energy product (BH) Reduction of the amount of content oxygen is very important for raising max. For this reason, these people discovered remarkable mineral oil and the synthetic oil of an operation which prevent advance of oxidation of said fines, collected and slurred said fines in these oils, fabricated this slurry, and proposed the manufacture process which can obtain the high performance R-Fe-B system sintered magnet of a hypoxia content and a high density mold by deoiling, sintering and heat-treating the Plastic solid subsequently acquired (reference, such as patent No. 2731337). This manufacture process is held at the low level equivalent to the R-Fe-B system alloy coarse powder before the amount of content oxygen of the R-Fe-B system sintered compact which has the description that advance of oxidation can be suppressed substantially, deoiled and sintered, and was obtained pulverizing by covering said impalpable powder and Plastic solid with said oil, and intercepting with atmospheric air. Therefore, R element in a R-Fe-B system sintered compact oxide-izes, reduction of the

amount of effective rare earth which dies out substantially and is produced is suppressed small, and the rare earth rich phase which forms a grain boundary phase is held healthfully. Since only a part with substantial small destruction of the amount of effective rare earth can set up R content low, compared with the former, excessive R rich phase and an excessive rare earth oxide can be reduced, and since the rate of a volume ratio of the $R_2Fe_{14}B$ mold crystal grain (the main phase) of a ferromagnetic phase is raised by coincidence, Br and (BH) max improve notably.

[0003]

[Problem(s) to be Solved by the Invention] However, the needs of a miniaturization and lightweight-izing of magnet application products, such as the latest VCM, and CD pickup, a motor for household electric appliances, are deep-rooted, and the demand of the formation of small size of the rare earth sintered magnet used and high-performance-izing is becoming still severer. Even if it applied said manufacture process (reference, such as patent No. 2731337) which can obtain the high performance R-Fe-B system sintered magnet of a hypoxia content and a high density mold to this demand, Br and (BH) max did not become high, so that this invention persons expected. As a result of this invention persons' investigating this phenomenon in a detail, the magnetic field stacking tendency of said slurry was not enough, and it turned out that it has left the room of amelioration. In view of this problem, this invention persons already collect said fines in the oil which comes to blend non-oxidizing quality oils, such as mineral oil, nonionic, or an anionic detergent by the predetermined ratio. The obtained slurry has and has a good magnetic field stacking tendency, and it fabricates among a magnetic field by this slurry. Subsequently, by performing sequential deoiling, sintering, and heat treatment, the knowledge of the rare earth sintered magnet which raised Br and (BH) max compared with the former being obtained was carried out, and it applied for the manufacture approach (application for patent No. 196345 [2000 to]).

[0004] this invention persons were except nonionic or an anionic detergent, and as a result of inquiring wholeheartedly in quest of the slurry modifier which can acquire effectiveness similar to them, they discovered that the below-mentioned lubricant was suitable as a slurry modifier. Thus, the technical problem which this invention tends to solve is a hypoxia content, and is offering the manufacture approach which can obtain the rare earth sintered magnet of the high performance which has a high sintered compact consistency and raised the amount of preferred orientation compared with the former. Moreover, the technical problem of this invention is a hypoxia content, and is offering the R-T-B system sintered ring magnet of high performance which has a high sintered compact consistency and raised the amount of preferred orientation of the polar-anisotropic direction or an parallel anisotropy compared with the former.

[0005]

[Means for Solving the Problem] The manufacture approach of the rare earth sintered magnet of this invention which solved the above-mentioned technical problem At least one sort of oils which pulverize the alloy coarse powder for rare earth sintered magnets in mean particle diameter of 1-10 micrometers in a non-oxidizing atmosphere, and are chosen from mineral oil, synthetic oil, and vegetable oil in the obtained fines, Collect in the non-oxidizing quality oil which consists of lubricant which consists of at least one sort chosen from from among the monohydric alcohol ester of a fatty acid, the monohydric alcohol ester of polybasic acid, the fatty acid ester of polyhydric alcohol, and those derivatives, and a slurry is produced. Subsequently, it is characterized by fabricating by said slurry, deoiling the acquired Plastic solid, sintering subsequently, and heat-treating.

[0006] Moreover, the ring magnet of this invention is weight %, and is R (R is at least one sort of the rare earth elements containing Y). Nd occupied to R is more than 50 atom % -- :28-33%, B:0.8 - 1.5%, Co:0.5-5%, and Cu: -- 0.01 to 0.3% And the remainder : It is the ring magnet which consists of a major component of Fe, and a R-Fe-Co-Cu-B system sintered magnet containing an unescapable impurity. The amount of oxygen contained unescapable to the total weight of said ring magnet is 0.3% or less. It has polar anisotropy and a consistency is more than 7.56 Mg/m³ (g/cm³). X diffraction peak intensity [from the field (105) observed in the magnetic pole period core surface location in a ring outer-diameter side]: -- I (105) and X diffraction peak

intensity [from a field (006)]: -- a ratio with I (006) is characterized by being $I(105)/I(006) = 0.5-0.8$. Said ring magnet has measured the ratio of X diffraction peak intensity: I (105) from the field by the X diffraction (105) which used CuK α 1 line ($\lambda = 0.15405\text{nm}$) for X line source, and X diffraction peak intensity: I (006) from a field (006), and can obtain high Br and high (BH) max compared with the former at the time of $I(105)/I(006) = 0.5-0.8$.

[0007] Moreover, the ring magnet of this invention is weight %, and is R (R is at least one sort of the rare earth elements containing Y). Nd occupied to R is more than 50 atom % -- :28-33%, B:0.8 - 1.5%, and Co: -- the major component of 0.5 - 5%, Cu:0.01-0.3%, and remainder:Fe -- And it is the ring magnet which consists of a R-Fe-Co-Cu-B system sintered magnet containing an unescapable impurity. The amount of oxygen contained unescapable to the total weight of said ring magnet is 0.3% or less. It has an parallel anisotropy and a consistency is more than 7.56 Mg/m³ (g/cm³). The coercive force iH_c of a room temperature is more than 1.1 MA/m (14kOe). The amount of preferred orientation which the residual magnetic flux density (Br//) of the direction of orientation in a room temperature and the residual magnetic flux density (Br**) of the die-length direction perpendicular to the direction of orientation define : $[(Br//) / (Br// + Br**) \times 100(\%)]$ It is characterized by being 85.5% or more.

[0008]

[Embodiment of the Invention] this invention persons examined the organic chemistry matter which consists of polar groups, such as -OH which a bias is in the lipophilic group which consists of a hydrocarbon chain (C_nH_m), and charge distribution of a chemical bond as lubricant for reforming of said slurry, and has an electric polarity, -COOH, -COO-, and >NH₂. If R-Fe-B system alloy fines are collected and slurred in the liquid which comes to blend mineral oil, synthetic oil or vegetable oil, and said lubricant at the rate of a Sadashige Tokoro quantitative ratio, the polar group of said lubricant will stick to said fines particle, and the lipophilic group of said lubricant will play the role of a protective coat. Although the source of the adsorption power is the electric attraction of a polar group, depending on the case, it may react with the configuration element of a R-Fe-B system alloy fines particle, and it may be chemisorbed. For this reason, it turned out that the number of admolecules per unit area to the strength [particle / said / lubricant and / fines] of adsorption and said fines particle front face changes with the classes of polar group, and the amount of carbon residue after the sintering process following a deoiling process and it changes notably. Moreover, even if it had the same polar group, when the carbon number of a lipophilic group increased, the molecular weight of lubricant itself became large, volatility became low, and the phenomenon which the amount of carbon residue increases was seen. In this way, this invention persons examined lubricant suitable for second solving the above-mentioned technical problem in the first place paying attention to the relation between the class of the relation between the class of a polar group and lipophilic group, and a R-Fe-B system sintered compact carbon content, a polar group, and lipophilic group, and magnetic properties in the detail. Consequently, the increment in a sintered compact content carbon content was suppressed very small, and the lubricant of the basic structure expression of [-izing 1] with which high iH_c can be obtained and the suitable high Plastic solid reinforcement for mass production is obtained was discovered. In [-izing 1], R1 and R1' are hydrocarbon groups.

[0009]

[Formula 1]

O R1'

|

R1- C = O

[0010] The polar group of the suitable lubricant for this invention is restricted to COO (ester bond), and the carbon number of a lipophilic group has desirable five or more piece 20 or less lubricant. A COO radical does not have one piece in 1 molecule of lubricant, and may be included two or more pieces here. moreover, the hydrocarbon chain (C_nH_m) of a lipophilic group -- two or more pieces -- containing -- **** (m and n are positive integers) -- the carbon number in one lipophilic group has five or more desirable pieces [20 or less]. It is difficult not to obtain

lubricity with the carbon content sufficient by less than five pieces in a lipophilic group, but to improve magnetic properties. Moreover, the carbon content in a lipophilic group becomes excessive [the molecular weight of lubricant] in 20-piece **, the boiling point goes up, volatility falls, and the amount of carbon residue causes the fall of iHc in super-** 0.1% of the weight. Or lubrication will become superfluous and Plastic solid reinforcement will be reduced. Any of saturation and partial saturation are sufficient as the hydrocarbon of a lipophilic group. Specifically, the lubricant used for this invention is at least one sort chosen from among the monohydric alcohol ester of a fatty acid, the monohydric alcohol ester of polybasic acid, the fatty acid ester of polyhydric alcohol, and those derivatives. The addition of lubricant is expressed with a ratio with R-Fe-B system alloy fines. As for the rate of a compounding ratio, it is desirable to consider as the (R-Fe-B system alloy fines) (lubricant) = 99.99-99.5 weight section:0.01 - 0.5 weight section, and its 99.99-99.7 weight section:0.01 - 0.3 weight section is more desirable. If the addition effectiveness is not acquired under in said range but the addition of lubricant exceeds said range, Plastic solid reinforcement and iHc will fall notably. In addition, since R-Fe-B system alloy fines and lubricant distribute good in a slurry and its magnetic field stacking tendency of a slurry improves while especially the combination weight ratio of said oil to R-Fe-B system alloy fines and lubricant is not limited but can cover everywhere a R-Fe-B system alloy fines front face, it is desirable. You may add to the R-Fe-B system alloy coarse powder before pulverizing, and it is the addition stage of lubricant at the slurry production time, and it may be added.

[0011] The following of the thing applicable as lubricant is carried out. For example, with the monohydric-alcohol ester of a fatty acid, there is methyl caprate, methyl myristate, methyl laurate, methyl stearate, OIREN acid methyl, or a thing that butyl, the propyl group, and the ethylhexyl radical attach instead of the methyl group of these ester. Moreover, with the monohydric-alcohol ester of polybasic acid, there are adipic-acid dioleoyl, diisodecyl adipate, diisobutyl adipate, phthalic acid ditridecyl ester, phthalic-acid 2-ethylhexyl, phthalic acid diisononyl ester, didecyl phthalate, phthalic-acid dialkyl, etc. Moreover, there is sorbitan trioleate etc. in the fatty acid of polyhydric alcohol, and its derivative. Although the direction of the monohydric-alcohol ester of a fatty acid or the monohydric-alcohol ester of polybasic acid is [some], it is easy to raise a magnetic stacking tendency rather than the fatty acid of polyhydric alcohol, and the thing of the derivative.

[0012] When the rare earth sintered magnet by this invention makes the main phase an $R_2Fe_{14}B$ intermetallic compound (R is at least one sort of the rare earth elements containing Y, and Nd occupied to R is more than 50 atom %), it is weight % about a major component presentation. R:28 - 33% . B:0.8 - 1.5% M 1:0 - 0.6% (M1 is at least one sort chosen from Nb, Mo, W, V, Ta, Cr, Ti, Zr, and Hf), It is desirable to carry out to M2:0-0.6% (at least one sort as which M2 is chosen from aluminum, Ga, and Cu), and Remainder Fe (however, when it to consider as $R+B+Fe+M1+M2=100$ % of the weight). Hereafter, only describing it as % shall mean weight %. 28 - 33% of the amount of R is desirable. Since good corrosion resistance is provided, 28 - 32% of the amount of R is more desirable, and is desirable. [especially 28 - 31% of] The amount of R cannot obtain predetermined iHc at less than 28%, but Br decreases remarkably by ** 33%. In order to obtain predetermined Br and the predetermined amount of preferred orientation, as for R, it is desirable to consist of Nd, Nd and Dy or Nd, Dy and Pr, and an unescapable R component. That is, it is desirable to carry out Nd occupied to R to more than 50 atom %, and to make Dy content 0.3 - 10%. Moreover, it is more desirable to carry out Nd occupied to R to more than 90 atom %, and to make Dy content 0.5 - 8%. The use of Nd with resource tops abundant [Nd occupied to R] at under 50 atom % is restricted, and practicality falls. At less than 0.3%, the content effectiveness of Dy is not acquired for Dy content, by **, Br falls 10% and the predetermined amount of preferred orientation cannot be obtained. 0.8 - 1.5% of the amount of B is desirable, and is more desirable. [0.85 - 1.2% of] It is difficult for the amount of B to obtain iHc more than 1.1 MA/m (14kOe) at less than 0.8%, and Br falls [the amount of B] remarkably by ** 1.5%. It is desirable in order that containing the refractory metal element M1 which consists of at least one sort of Nb, Mo, W, V, Ta, Cr, Ti, Zr, and Hf 0.01 to 0.6% may raise magnetic properties. By containing M1 0.01 to 0.6%, too much grain growth of the main phase

crystal grain in a sintering process is controlled, it is stabilized and iH_c more than 1.1 MA/m (14kOe) can be obtained. However, if M1 is super-contained 0.6%, normal grain growth of the main phase crystal grain will be checked conversely, and the fall of Br will be caused. Moreover, the effectiveness that M1 content improves magnetic properties at less than 0.01% is not acquired. 0.01 – 0.6% of the content of M2 element (at least one sort of aluminum, Ga, and Cu) is desirable. Although iH_c improves by content of aluminum and corrosion resistance is improved, the effectiveness that Br falls greatly by ** 0.6%, and aluminum content raises iH_c and corrosion resistance at less than 0.01% is not acquired. More desirable aluminum content is 0.05 – 0.3%. Although iH_c improves notably by content of Ga, the effectiveness that Br falls greatly by ** 0.6%, and Ga content raises iH_c at less than 0.01% is not acquired. More desirable Ga content is 0.05 – 0.2%. Although minute amount addition of Cu contributes to a corrosion resistance improvement and improvement in iH_c , the effectiveness that Br falls greatly by ** 0.3%, and Cu content raises corrosion resistance and iH_c at less than 0.01% is not acquired. More desirable Cu content is 0.05 – 0.3%. Although corrosion resistance is improved by content of Co, the Curie point goes up and the thermal resistance of a rare earth sintered magnet improves, a Fe-Co phase with Co content harmful to magnetic properties in 5% ** is formed, or R2 (Fe, Co) 14 B phase is formed, and Br and iH_c fall greatly. Therefore, 5% or less of Co content is desirable. On the other hand, at less than 0.5%, the improvement effectiveness corrosion resistance [content / Co] and heat-resistant is not acquired. Therefore, 0.5 – 5% of Co content is desirable. When 0.5 – 5% and Cu are contained for Co 0.01 to 0.3%, the effectiveness that the allowable temperature of the second heat treatment which can obtain iH_c of the room temperature more than 1.1 MA/m (14kOe) spreads can be acquired, and it is especially desirable. If aluminum is made to contain 0.01 to 0.3%, while contributing to the improvement in coercive force, it is possible to reduce fluctuation of the coercive force by dispersion in heat treatment temperature. Moreover, if Nb is made to contain 0.01 to 0.08%, the grain growth in a sintering process can be controlled and formation of a big and rough grain can be controlled. 0.3% or less of the amount of oxygen contained impossibly is desirable, is more desirable, and is desirable. [especially 0.18% or less of] [0.2% or less of] A sintered compact consistency can be raised to abbreviation theoretical density by reducing an oxygen content to 0.3% or less. if the sintered compact consistency more than 7.56 Mg/m³ (g/cm³) is stabilized and obtained in the case of the R-Fe-B system sintered magnet which makes the main phase an R₂Fe₁₄B mold intermetallic compound and a major component presentation, pulverizing mean particle diameter, sintering temperature, etc. are chosen further suitably --- more than 7.58 Mg/m³ (g/cm³) -- further -- the thing more than 7.59 Mg/m³ (g/cm³) can be obtained. Moreover, 0.10% or less of the carbon content contained impossibly is desirable, and is more desirable. [0.07% or less of] Generation of rare earth carbide is suppressed by reduction of a carbon content, the amount of effective rare earth increases, and iH_c , (BH) max, etc. can be raised. Moreover, 0.15% of the nitrogen volume contained impossibly is desirable. If nitrogen volume exceeds 0.15%, Br will fall greatly. Although well-known surface treatment coats (nickel plating etc.) are covered by the magnet of this invention and practical use is presented, the amount of R is 28 – 32%, and since good corrosion resistance is given when nitrogen volume is 0.002 – 0.15%, it is more desirable. Moreover, when the magnet of this invention is produced using what was produced by the reduction diffusion method which uses calcium as a reducing agent as a raw material alloy, in order to obtain predetermined iH_c and the predetermined amount of preferred orientation, it is desirable to stop calcium content to 0.1 or less (for 0 not to be included) % of the weight, using total weight of said magnet as 100 % of the weight, and it is more desirable to stop to 0.03 or less (for 0 not to be included) % of the weight.

[0013] What makes the main phase SmCo₅ or Sm₂TM₁₇ (TM consists of Co, Fe, Cu, and M', and M' is at least one sort chosen from Zr, Hf, Ti, and V) is included by the rare earth sintered magnet by this invention.

[0014] Pulverizing of the raw material alloy in the manufacture approach of the rare earth sintered magnet of this invention can be performed using wet-grinding equipments, such as a wet ball mill set as the conditions which can prevent the dry grinding equipment or oxidization by the jet mill which uses inert gas as tumbling media. For example, under 0.1 volume %, an oxygen

density collects and slurs direct fines out of said inert gas ambient atmosphere in the non-oxidizing quality liquid which consists of at least one sort of oils chosen from the mineral oil, synthetic oil, and vegetable oil of the rate of a predetermined compounding ratio, and lubricant so that atmospheric air cannot be more preferably touched after jet mill pulverizing in the inert gas ambient atmosphere below 0.01 volume %. The mean particle diameter of said fines has desirable 1–10 micrometers, and its 3–6 micrometers are more desirable. By less than 1 micrometer, the efficiency of comminution of fines falls [mean particle diameter] greatly, and μ Hc and the amount of preferred orientation fall greatly in 10-micrometer **. It fabricates among a magnetic field with predetermined shaping equipment by using the collected slurry as a shaping raw material. In order to prevent degradation of the magnetic properties by oxidation of a Plastic solid, it is desirable to save in said liquid from immediately after shaping to deoiling. If the temperature up of the Plastic solid is rapidly carried out from ordinary temperature to sintering temperature, the internal temperature of a Plastic solid rises rapidly, the oil which remains to a Plastic solid, and the rare earth elements which constitute a Plastic solid will react, rare earth carbide will be generated, and magnetic properties will deteriorate. It is desirable to perform deoiling processing heated more than for 30 minutes with the temperature of 100–500 degrees C and below the degree of vacuum of 13.3Pa (10–1Torr) as this cure. The oil which remains to a Plastic solid by deoiling processing is fully removed. In addition, as long as it is 100–500 degrees C, whenever [stoving temperature / of deoiling processing] does not need to be one point, and may be two or more points. Moreover, deoiling is efficiently performed also by performing deoiling processing which makes the following hereafter the programming rate from a room temperature to 500 degrees C by 5-degree-C/more preferably by 10-degree-C/below by 13.3Pa (10–1Torr). [0015] A thing 350 degrees C or less has a point to the good point of deoiling and a moldability distilling fractionally as a pulp oil, synthetic oil, or vegetable oil. Moreover, the thing of 10 or less cSts has the good kinematic viscosity of a room temperature, and the thing of 5 or less cSts is still more desirable.

[0016]

[Example] Hereafter, this invention is not limited by these examples although an example explains this invention.

(Example 1) weight % -- Nd:23.1%, Pr:6.4%, and Dy: -- 1.0%, B:0.9%, Co:2.0%, Ga:0.1%, Cu:0.1%, and remainder:Fe from -- the becoming R-Fe-B system alloy coarse powder Jet mill pulverizing is carried out in the nitrogen-gas-atmosphere mind which the oxygen density adjusted to 10 ppm or less by the volume ratio. Fines with a mean particle diameter of 4.0 micrometers obtained were collected and slurred in mineral oil (the Idemitsu Kosan make, trade name:Idemitsu super sol PA-30), without touching atmospheric air in this nitrogen-gas-atmosphere mind. In addition, mean particle diameter was measured with the laser diffraction mold particle-size-distribution measuring device (trade name: HEROSU Rhodes) made from Sympatec. Subsequently, the methyl oleate of the specified quantity was added to the obtained slurry, and it mixed with the agitator. the combination items of a slurry -- said fines: -- it considered as 70 weight sections, the mineral oil:29.9 weight section, and the methyl oleate:0.10 weight section. This slurry is injected into a predetermined metal mold cavity, and they are orientation magnetic-field-strength:1.0 MA/m (13kOe) and compacting pressure. : Compression molding of a horizontal magnetic field was performed on condition that 98MPa (1.0 ton/cm²), and the Plastic solid of the shape of a 15mmx25mmx10mm rectangular parallelepiped was acquired. Moreover, the direction of orientation was made into the direction of 10mm [about]. The room temperature reinforcement of this Plastic solid was measured by the three-point bending test. In addition, it set to the fixture of a bending tester so that the 15mmx25mm field of a Plastic solid might turn into a vertical side, and it pressurized in parallel with the 10mm side, and three-point flexural strength was measured. A result is shown in Table 1. Moreover, on the degree of vacuum of about 66.5Pa (5x10–1Torr), and 200-degree C conditions, another Plastic solid fabricated similarly was heated for 3 hours, and was deoiled, and, subsequently the temperature up was carried out to 1050 degrees C in this ambient atmosphere, and subsequently, at 1050 degrees C, it held for 2 hours, sintered and cooled to the room temperature after that. The first heat treatment which heats the obtained sintered compact at 900 degrees C in argon atmosphere for

2 hours, and subsequently quenches it to a room temperature was performed, continuously, it heated at 480 degrees C in argon atmosphere for 1 hour, and the second heat treatment subsequently cooled to a room temperature was performed, and the R-Fe-B system sintered magnet of about 10mm angle was obtained. The obtained sintered magnet was processed into 7mm angle, and it considered as the magnetic-properties test sample. Next, in the room temperature (20 degrees C), the pulse magnetic field of 11.9 MA/m (150kOe) was impressed along the anisotropy grant direction of said sample, and magnetic properties were measured. Magnetic properties calculated the maximum ($4\pi i_{lmax}$) of the intensity of magnetization when impressing the pulse magnetic field of 11.9 MA/m, and defined and evaluated the amount of preferred orientation by ($Br / 4\pi i_{lmax}$). A result is shown in Table 1. Moreover, the analysis value of the content carbon content of the obtained sintered magnet is shown in Table 1.

(Examples 2-4) Three sorts each of slurries were produced like the example 1 except having added respectively methyl stearate, diisodecyl adipate, and stearin acid 2-ethylhexyl instead of methyl oleate. Each R-Fe-B system sintered magnet was produced and evaluated like the example 1 except having used this slurry after that. A result is shown in Table 1.

(Example 1 of a comparison) The slurry which consists of the R-Fe-B system fines and mineral oil of an example 1 was produced without adding methyl oleate, and the R-Fe-B system sintered magnet was produced and evaluated like the example 1 except having used this slurry after that. A result is shown in Table 1.

(Example 2 of a comparison) It changed to methyl oleate, and the same procedure as an example 1 produced and estimated the R-Fe-B system sintered magnet to the slurry of an example 1 except having carried out 0.1 weight section addition of the oleyl alcohol. A result is shown in Table 1.

(Example 3 of a comparison) It changed to methyl oleate, and the same procedure as an example 1 produced and estimated the R-Fe-B system sintered magnet to the slurry of an example 1 except having carried out 0.1 weight section addition of the oleyl amine. A result is shown in Table 1.

(Example 4 of a comparison) It changed to methyl oleate, and the same procedure as an example 1 produced and estimated the R-Fe-B system sintered magnet to the slurry of an example 1 except having carried out 0.1 weight section addition of the methyl acetate. A result is shown in Table 1.

(Example 5 of a comparison) It changed to methyl oleate, and the same procedure as an example 1 produced and estimated the R-Fe-B system sintered magnet to the slurry of an example 1 except having carried out 0.1 weight section addition of the behenic acid methyl. A result is shown in Table 1.

[0017] Although the Plastic solid reinforcement of an example 1 was a little low compared with the example 1 (lubricant additive-free) of a comparison, it was proved that it was the level which does not generate a problem at all on industrial production. A lipophilic group is the same (17 carbon numbers) respectively, and, as for the methyl oleate of an example 1, the oleyl alcohol of the example 2 of a comparison, and the oleyl amine of the example 3 of a comparison, only polar groups differ (they are $-COO-$, $-OH$, and $>NH_2$ to order). It turns out that it depends for Plastic solid reinforcement on the class of polar group of lubricant so that clearly from an example 1 and the examples 2 and 3 of a comparison. Moreover, although the amount of preferred orientation ($Br/4\pi i_{lmax}$) of magnetic properties is all comparable in an example 1 and the examples 2 and 3 of a comparison, compared with an example 1, iHc of the examples 2 and 3 of a comparison is falling. If based on the example 1 of a comparison, a sintered compact carbon content increases by the residual of the added lubricant, and since extent to which iHc falls differs, a sintered compact carbon content will also be judged to be dependent on the class of polar group. Moreover, the examples 4 and 5 of a comparison make the polar group of lubricant $-COO-$, and change the carbon number of the hydrocarbon chain in a lipophilic group. Since the improvement of the amount of preferred orientation ($Br/4\pi i_{lmax}$) is not accepted from the result of the example 4 of a comparison when a hydrocarbon chain is short, it is judged that it has not contributed on the lubrication disposition between said fines. On the other hand, although the amount of preferred orientation ($Br/4\pi i_{lmax}$) is seen from the example 5 of a comparison when a

hydrocarbon chain is long, a sintered compact carbon content increases and it turns out that the fall of iHc is large.

[0018]

[Table 1]

	潤滑剤	親油基中の炭素数 (個)	$Br/4\pi l_{max}$ (%)	(BH)max (kJ/m ³) (MGoe)	iHc (MA/m) (kOe)	焼結体炭素量 (wt%)	成形体強度 (MPa)
実施例 1	オレイン酸メチル	17	96.5	395 49.4	1.23 15.4	0.067	0.81
実施例 2	ステアリン酸メチル	17	96.2	391 49.1	1.23 15.4	0.067	0.81
実施例 3	アジピン酸ジイソデシル	20	96.7	394 49.5	1.23 15.5	0.067	0.79
実施例 4	ステアリン酸 2-エチルヘキシル	25	96.4	392 49.2	1.22 15.3	0.068	0.79
比較例 1	無添加	—	95.1	377 47.4	1.23 15.5	0.065	1.34
比較例 2	オレイルアルコール	17	96.3	390 49.0	1.17 14.7	0.088	0.34
比較例 3	オレイルアミン	17	96.0	389 48.9	1.15 14.4	0.089	0.37
比較例 4	酢酸メチル	1	95.2	379 47.6	1.23 15.5	0.066	—
比較例 5	ヘパニン酸メチル	22	96.8	395 49.6	1.14 14.3	0.093	—

[0019] The R-T-B system sintered ring magnet which has polar anisotropy is produced to below, and the evaluated example is explained to it.

A major component presentation by weight % Nd:23.1%, Pr:6.4%, Dy:1.0%, B:1.05%, (Example 5) An oxygen density carries out jet mill grinding of the R-Fe-B system raw material alloy coarse powder (320-mesh undershirt) which consists of Ga:0.08%, Nb:0.2%, aluminum:0.05%, Cu:0.13%, Co:2.0%, and the remainder Fe in less than (volume ratio) 1 ppm nitrogen-gas-atmosphere mind. The slurry was produced like the example 1 except having used fines with a mean particle diameter of 3.8 micrometers obtained. After filling up the cavity 59 of the making machine which shows the obtained slurry to drawing 1, it fabricated among the magnetic field so that compacting pressure:78.4MPa (0.8 ton/cm²) and the pulse magnetic field of 100V might make polar-anisotropic, and the Plastic solid was acquired. The Plastic solid was heated for 1 hour on the conditions whose degree of vacuums are about 66.5Pa (5x10⁻¹Torr) and 200 degrees C, after deoiling, it cooled to the after [2 hour sintering] room temperature continuously on about 4.0x10 to 3 Pa (3x10⁻⁵Torr), and 1060-degree C conditions, and the sintered compact was obtained. Next, heat treatment which cools to 550 degrees C after 1-hour heating at 900 degrees C in argon atmosphere, and is subsequently further cooled to a room temperature after 2-hour heating at 550 degrees C was performed. Next, the epoxy resin film of 12 micrometers of average thickness was coated according to electrodeposition after processing a predetermined dimension, and the polar-anisotropic ring which has the polar anisotropy of eight poles with the outer diameter of 48mm, a bore [of 30mm], and a height of 11mm was obtained. Next, the sample for X diffractions was started so that the magnetic pole period center section in the outer-diameter side of the above-mentioned polar-anisotropic ring could be measured, the sample was set in the X-ray diffractometer made from Physical science Electrical and electric equipment (RU-200BH), and the X diffraction was carried out by the 2 theta-theta scanning method. To X line source, the software built in equipment removed the noise (background) using CuKalpha1 line (lambda= 0.15405nm). It was the 2theta=29.08 degree field (004) of the R2T14B mold intermetallic compound which is the main phase, a 38.06 degrees field (105), and a 44.34-degree field (006), and the main diffraction peaks made 100% X diffraction peak intensity:I (006)

from a field (006), and were $I(004) / I(006) = 0.33$, and $I(105) / I(006) = 0.63$. A result is shown in Table 2.

(Example 6 of a comparison) It changed to the slurry of an example 5 and the polar-anisotropic ring of the example of a comparison was produced like the example 5 except having fabricated among the magnetic field in the polar-anisotropic direction by the slurry of the example 1 of a comparison. The X diffraction of the polar-anisotropic ring of the example 6 of a comparison as well as an example 5 was performed henceforth. A result is shown in Table 2. Although the main diffraction peaks were the same as an example 5, it was $I(004) / I(006) = 0.32$, and $I(105) / I(006) = 0.96$. Moreover, the amount of oxygen of said polar-anisotropic ring was 0.13 % of the weight, the carbon content was 0.05 % of the weight, and nitrogen volume was 0.003 % of the weight.

[0020]

[Table 2]

	密度 (Mg/m ³) (g/cm ³)	Bo (T) (kG)	I(105)/ I(006)
実施例 5	7.59	5.80 58.0	0.63
比較例 6	7.59	5.48 54.8	0.96

[0021] According to this invention, from the result of the example 5 of Table 4, and the example 6 of a comparison, it has polar anisotropy. The ratio of X diffraction peak intensity: $I(105)$ from a field (105) and X diffraction peak intensity: $I(006)$ from a field (006) which a consistency is more than 7.56 Mg/m³ (g/cm³), and were observed in the magnetic pole period core surface location in a ring outer-diameter side It turns out that the polar-anisotropic ring which is $I(105)/I(006) = 0.5-0.8$ can be offered.

[0022] The whole produces to below the R-T-B system sintered ring magnet which carried out orientation to the one direction to the axial perpendicular direction (it is henceforth called an parallel anisotropy), and explains the evaluated example to it.

(Example 6) The slurry was produced like the example 1. compacting pressure: 78.4MPa (0.8 ton/cm²) and an axial perpendicular direction after filling up the cavity 59 (the bore of dices 51 and 52: mm [60], outer-diameter: 45mm [of a core 53], die-length: 34mm [of the dice ferromagnetism section 51], restoration depth: 34mm) of the making machine which shows the obtained slurry to drawing 1 -- an one direction -- magnetic-field-strength: -- it fabricated on the conditions to which about 238.7 kA/m (3kOe) was applied among the magnetic field, and the Plastic solid was acquired. The parallel anisotropy ring which has an parallel anisotropy like an example 5 was obtained henceforth. Next, as shown in drawing 2, it started along the direction of orientation of said produced parallel anisotropy ring 70, and the rectangular parallelepiped of the 2.8mm of the directions of the diameter of 6.5mm [of the 5mm x die-length directions of tangential directions] x was obtained. Drawing 2 (b) explains the logging point of a rectangular parallelepiped. A straight line OPQ is drawn from the central point O of the parallel anisotropy ring 70 at right angles to the direction of orientation to radial. Point P is a contact with inner skin, and Point Q is a contact with a peripheral face. Next, the tangent RPS in Contact P is drawn and it is made for the die length of Tangent RPS to be set to 5mm focusing on Contact P. Next, a straight line RT (die length of 2.8mm) and a straight line SU (die length of 2.8mm) are drawn at right angles to Tangent RPS. Next, a straight line TU (die length of 5mm) is drawn in parallel with Tangent RPS. The direction of RPS and the TU direction in a rectangle RSUT are a tangential direction of the parallel anisotropy ring 70, and the direction of RT and the SU direction are defined as the direction of orientation of the parallel anisotropy ring 70. Moreover, the thickness direction of a rectangle RSUT is the die-length direction of the parallel anisotropy ring 70, and started in die length of 6.5mm. After starting a total of four rectangular parallelepipeds by this logging point, each of those directions were made in agreement and the rectangular parallelepiped stuck and united was obtained. The following magnetic properties were

measured by this rectangular parallelepiped. In addition, what is necessary is to make each of those directions in agreement, to stick and unite, and just to adjust a dimension, after starting two or more rectangular parallelepipeds according to the aforementioned logging point except that dimensions differ when the rectangular parallelepiped of said dimension cannot be started from the parallel anisotropy ring of the measuring object. The residual magnetic flux density ($Br//$), the coercive force iHc , maximum energy product $(BH)_{max}$, and the remanence ratio (Hk/iHc) of the direction of orientation in the room temperature (20 degrees C) of said rectangular parallelepiped were measured. Hk is the value of H equivalent to $0.9Br$ in the 2nd quadrant of a $4\pi i$ (intensity of magnetization)– H (magnetic field strength) curve, and the remanence ratio (Hk/iHc) which $**ed$ Hk by iHc shows the rectangle nature of a $4\pi i$ – H demagnetization curve. Next, it asked for the amount of preferred orientation of the parallel anisotropy ring defined by $[(Br//) / (Br// + Br**) \times 100(\%)]$ after measuring the residual magnetic flux density ($Br**$) of the die-length direction in the room temperature (20 degrees C) of said rectangular parallelepiped. The consistency of an parallel anisotropy ring was measured again. Those measurement results are shown in Table 3. Moreover, the amount of oxygen of said parallel anisotropy ring was 0.13 % of the weight, the carbon content was 0.05 % of the weight, and nitrogen volume was 0.003 % of the weight.

(Example 7 of a comparison) It changed to the slurry of an example 5, and the parallel anisotropy ring of the example of a comparison was produced and evaluated like the example 5 except having fabricated among the magnetic field in the direction of orientation by the slurry of the example 1 of a comparison. A result is shown in Table 3.

[0023]

[Table 3]

	密度 (Mg/m^3) (g/cm^3)	$Br//$ (T) (kG)	iHc (MA/m) (kOe)	$(BH)_{max}$ (kJ/m^3) (MGOe)	(Hk/iHc) (%)	配向度 (%)
実施例 6	7.60	1.35 13.5	1.27 16.0	353.3 44.4	96.4	92.3
比較例 7	7.60	1.31 13.1	1.31 16.5	319.9 40.2	87.1	89.4

[0024] According to this invention, a consistency from the result of the example 6 of Table 3, and the example 7 of a comparison Three or more 7.56 g/cm, iHc more than 1.25T (12.5kG) More than 1.1 MA/m (14.0kOe) [$Br//$ in the direction of orientation] (BH) It turns out that max can offer the parallel anisotropy ring which has the high magnetic properties of [(Hk/iHc)] 85.5% or more in the amount of preferred orientation of 87.5% or more and the direction of orientation which are not in the former more than 282.6 kJ/m³ (35.5MGOe).

[0025] The R–T–B system sintering arc segment magnet which has an parallel anisotropy as other examples is produced to below, and the evaluated example is explained to it.

(Example 7) The raw material tank 13 of the slurry feeder 15 of drawing 3 was filled up with the slurry produced in the example 1. Next, the slurry supply pipe 6 was dropped in the cylinder (illustration abbreviation), and it was made to stop in the location near the base of the cavity 3 of an arc segment configuration (location near the top face of bottom punch 2). Next, the pump 10 was operated, the slurry supply pipe 6 was gone up from the raw material tank 13 to the upper limit section location of a cavity 3 in the cylinder (illustration abbreviation) with discharge from the slurry supply pipe 6 to the cavity 3 through piping 11 in the slurry, and the cavity 3 was filled up with the slurry of the specified quantity. Subsequently, after raising the slurry supply pipe 6 in the cylinder (illustration abbreviation) and drawing out from a cavity 3, the supply head 9 was moved leftward in the cylinder 4, the pressure of 98MPa(s) (1 ton/cm²) was applied by upper punch (illustration abbreviation) and bottom punch 2, horizontal magnetic field compression molding was performed, impressing the orientation magnetic field of 1.0 MA/m (13kOe) horizontally subsequently, and the arc segment Plastic solid was acquired. It sintered after deoiling a Plastic solid like the example 1, and heat-treated henceforth. Subsequently, it is processed until the sintering skin of the obtained sintered magnet material front face is lost, and subsequently it comes to coat the epoxy resin film of 15 micrometers of average film pressure.

thickness T shown in drawing 4 -- $1 = 2.8\text{mm}$, die-length $L1 = 80.0\text{mm}$, and a central angle -- the R-Fe-B system sintering arc segment magnet 30 of $\theta_1 = 45$ degree thin meat and a long configuration was obtained. The curvature of the $L1$ direction of said material before processing was less than 1mm , was small, and was good. [of the amount of preferred orientation ($Br/4\pi I_{\text{max}}$) of the anisotropy grant direction] The anisotropy of the arc segment sintered magnet 30 is given in the ** direction (it is perpendicularly mostly to space). As a result of starting a sample from said arc segment magnet 30 and measuring the magnetic properties of the magnetic-anisotropy grant direction at a room temperature (20 degrees C), the high value of $iH_c = 1.24 \text{ MA/m}$ (15.6kOe) and $(BH)_{\text{max}} = 394.8 \text{ kJ/m}^3$ (49.6MGOe) was acquired amount-of-preferred-orientation ($Br/4\pi I_{\text{max}}$) = 96.8% . Moreover, the consistencies were 7.60 Mg/m^3 (g/cm^3), and the amount of oxygen was [0.05% of the weight and nitrogen volume of the carbon content] 0.02% of the weight 0.14% of the weight. Moreover, a sample is set in the X-ray diffractometer made from Physical science Electrical and electric equipment (RU-200BH). The result which carried out the X diffraction (CuKalpha1 line; $\lambda = 0.15405\text{nm}$ is used) by the 2 theta-theta scanning method, The $2\theta = 29.08$ degree field (004) of the R2T14B mold intermetallic compound whose main diffraction peaks are the main phases, a 38.06 -degree field (105), And it was a 44.34 -degree field (006) and was $I(105) / I(006) = 0.66$, having used X diffraction peak intensity: $I(006)$ from a field (006) as 100% .

[0026] (Example 8) The sintering arc segment magnet of thin meat and a long configuration which has the die length $L1$ of Table 2 and the dimension of thickness $T1$ and θ_1 was produced like the example 7 except having changed the thickness of a cavity 3, and the fill of a slurry. These magnets had the high magnetic properties of $iH_c = 1.23 - 1.25 \text{ MA/m}$ ($15.4 - 15.7\text{kOe}$) and $(BH)_{\text{max}} = 393.2 - 395.6 \text{ kJ/m}^3$ ($49.4 - 49.7\text{MGOe}$) amount-of-preferred-orientation ($Br/4\pi I_{\text{max}}$) = $96.4 - 96.7\%$ of the magnetic-anisotropy grant direction, the consistency was 7.60 Mg/m^3 (g/cm^3), and the amount of oxygen was [0.06% of the weight and nitrogen volume of the carbon content] $0.02 - 0.03\%$ of the weight 0.13 to 0.14% of the weight. Moreover, as a result of carrying out an X diffraction like the case of an example 7, it was $I(105)/I(006) = 0.67 - 0.68$. (Example 8 of a comparison) Although the horizontal magnetic field fabricating method was applied like the example 7 except having used the slurry of the example 1 of a comparison as the shaping raw material and shaping of the $T = 1.0 - 4.0\text{mm}$ Plastic solid for R-Fe-B system sintering arc segment magnets was tried, the crack occurred in the Plastic solid and a healthy Plastic solid without a crack was not able to be acquired.

[0027]

[Table 4]

	L_1 (mm)	T_1 (mm)	θ_1 (°)
実施例 8	7 2	1 . 0	5 5
		2 . 1	
		4 . 0	

[0028] The R-T-B system sintering arc segment magnet which has a radial anisotropy is produced to below, and the evaluated example is explained to it.

(Example 9) The inside diameter and radial orientation magnetic field strength (H_{ap}) of the Plastic solid for arc segment sintered magnets which have a radial anisotropy were changed, the sintering arc segment magnet 40 of drawing 5 which finally has the bore of die-length $L2 = 65\text{mm}$, thickness $T2 = 2.5\text{mm}$, $\theta_2 = 40$ degree, and Table 3 was produced, and relation with the amount of preferred orientation (%) of a bore, H_{ap} , and a radial direction was investigated. Results of an investigation are shown in Table 3. In addition, manufacture of this arc segment sintered magnet performed sequential deoiling, sintering, heat treatment, processing, and surface treatment like the example 7 except having changed the process condition and the Plastic solid dimension. It turns out that it has the amount of preferred orientation with a radial direction higher than Table 3. Moreover, as for those with 87.5% super-**, and iH_c , each arc segment magnet of Table 3 was [the remanence ratio (H_k/iH_c) of those with 1.1 MA/m (14kOe) super-** and the amount of oxygen] $0.13 - 0.14\%$ of the weight, the carbon content was $0.05 - 0.06\%$ of the weight, and nitrogen volume was $0.003 - 0.004\%$ of the weight.

(Example 9 of a comparison) Other than having used the slurry of the example 1 of a comparison as the shaping raw material, although shaping of the Plastic solid for sintering arc segment magnets which has the same configuration as an example 9 was tried, the Plastic solid crack occurred and a sintering arc segment magnet was not able to be produced.

[0029]

[Table 5]

アークセグメント 内径 (mm)	Hap (kA/m) (kOe)	配向度 (%)
100	708.3 8.9	92.6
50	612.8 7.7	92.2
30	461.6 5.8	91.9
10	310.4 3.9	91.7

[0030] Next, the example of a radial ring is explained.

A major component presentation by weight % Nd:21.4%, Pr:6.0%, Dy:3.1%, B:1.05%, (Example 10) An oxygen density carries out jet mill grinding of the R-Fe-B system raw material alloy coarse powder (320-mesh undershirt) which consists of Ga:0.08%, Nb:0.2%, aluminum:0.05%, Cu:0.13%, Co:2.0%, and the remainder Fe in less than (volume ratio) 1 ppm argon atmosphere. The slurry was produced like the example 1 except having used fines with a mean particle diameter of 3.8 micrometers obtained. Orientation magnetic field strength of the compacting-pressure:78.4MPa (0.8 ton/cm²) and a radial direction after filling up the cavity 59 (the bore of dices 51 and 52:mm [60], outer-diameter:45mm [of a core 53], die-length:34mm [of the dice ferromagnetism section 51], restoration depth:34mm) of the making machine which shows the obtained slurry to drawing 1 : It fabricated on the conditions of about 238.7 kA/m (3kOe) among the radial magnetic field, and the Plastic solid was acquired. The Plastic solid was heated for 1 hour on the conditions whose degree of vacuums are about 66.5Pa (5x10⁻¹Torr) and 200 degrees C, after deoiling, it cooled to the after [2 hour sintering] room temperature continuously on about 4.0x10 to 3 Pa (3x10⁻⁵Torr), and 1060-degree C conditions, and the sintered compact was obtained. Next, heat treatment which cools to 550 degrees C after 1-hour heating at 900 degrees C in argon atmosphere, and is subsequently further cooled to a room temperature after 2-hour heating at 550 degrees C was performed. Next, the epoxy resin film of 12 micrometers of average thickness was coated according to electrodeposition after processing a predetermined dimension, and the radial ring which has a radial anisotropy with the outer diameter of 48mm, a bore [of 39mm], and a height of 11mm was obtained. Next, as shown in drawing 2 , the rectangular parallelepiped of 2.8mm of 6.5mm x radial directions of the 5mm x die-length directions of tangential directions was started from the location of the arbitration of said produced radial ring 70. Drawing 2 (b) explains the logging point of a rectangular parallelepiped. A straight line OPQ is drawn from the central point O of the radial ring 70 to radial. Point P is a contact with inner skin, and Point Q is a contact with a peripheral face. Next, the tangent RPS in Contact P is drawn and it is made for the die length of Tangent RPS to be set to 5mm focusing on Contact P. Next, a straight line RT (die length of 2.8mm) and a straight line SU (die length of 2.8mm) are drawn at right angles to Tangent RPS. Next, a straight line TU (die length of 5mm) is drawn in parallel with Tangent RPS. The direction of RPS and the TU direction in a rectangle RSUT are a tangential direction of the radial ring 70, and the direction of RT and the SU direction are defined as the radial direction of the radial ring 70. Moreover, the thickness direction of a rectangle RSUT is the die-length direction of the radial ring 70, and started in die length of 6.5mm. After starting a total of four rectangular parallelepipeds by this logging point, each of those directions were made in agreement and the rectangular parallelepiped stuck and united was obtained. The following magnetic properties were measured by this rectangular

parallelepiped. In addition, what is necessary is to make each of those directions in agreement, to stick and unite, and just to adjust a dimension, after starting two or more rectangular parallelepipeds according to the aforementioned logging point except that dimensions differ when the rectangular parallelepiped of said dimension cannot be started from the radial ring of the measuring object. The residual magnetic flux density ($Br//$), the coercive force iHc , maximum energy product $(BH)_{max}$, and the remanence ratio (Hk/iHc) of the radial direction in the room temperature (20 degrees C) of said rectangular parallelepiped were measured. Hk is the value of H equivalent to $0.9Br$ in the 2nd quadrant of a $4\pi i$ (intensity of magnetization)– H (magnetic field strength) curve, and the remanence ratio (Hk/iHc) which Hk by iHc shows the rectangle nature of a $4\pi i$ – H demagnetization curve. Next, it asked for the amount of preferred orientation of the radial ring defined by $[(Br//) / (Br// + Br^{**}) \times 100(\%)]$ after measuring the residual magnetic flux density (Br^{**}) of the die-length direction in the room temperature (20 degrees C) of said rectangular parallelepiped. Moreover, the consistency of a radial ring was measured. Those measurement results are shown in Table 4. Moreover, the amount of oxygen of said radial ring was 0.13 % of the weight, the carbon content was 0.05 % of the weight, and nitrogen volume was 0.003 % of the weight.

(Example 10 of a comparison) It changed to the slurry of an example 10, and the radial ring of the example of a comparison was produced and evaluated like the example 10 except having fabricated among the radial magnetic field by the slurry of the example 1 of a comparison. A result is shown in Table 4.

[0031]

[Table 6]

	密度 (Mg/m^3) (g/cm^3)	$Br//$ (T) (kG)	iHc (MA/m) (kOe)	$(BH)_{max}$ (kJ/m^3) (MGOe)	(Hk/iHc) (%)	配向度 (%)
実施例 10	7.61	1.30 13.0	1.43 18.0	318.4 40.0	96.4	89.9
比較例 10	7.61	1.23 12.3	1.43 18.0	281.0 35.3	87.1	85.2

[0032] According to this invention, a consistency from the result of the example 10 of Table 4, and the example 10 of a comparison Three or more 7.56 g/cm, $Br//$ in a radial direction More than 1.25T (12.5kG) $(BH)_{max}$ more than 1.1 MA/m (14.0kOe) More than 282.6 kJ/m³ (35.5MGOe) [iHc] It turns out that (Hk/iHc) can offer the radial ring which has the high magnetic properties of 85.5% or more in the amount of preferred orientation of 87.5% or more and a radial direction which are not in the former.

[0033] (Example 11) The inside diameter of the Plastic solid ring which the dices 51 and 52 of the making machine of drawing 1 and the dimension of core 53 grade are changed, and has a radial anisotropy was changed, and the relation between the bore of Hap when changing radial orientation magnetic field strength (Hap) and the radial ring finally obtained and the amount of preferred orientation (%) of a radial direction was investigated. Hap falls, so that the bore of the Plastic solid ring, i.e., a radial ring, which has a radial anisotropy becomes small, as shown in Table 5. 716.2 kA/m (9kOe) of Hap in case the bore of a radial ring is 100mm was upper limits by generation of heat of the power source for magnetic field generating, and a coil etc. Except having considered as the radial magnetic field process condition which changed the bore of said Plastic solid ring, an outer diameter (outer diameter = bore + (8–20mm)), and Hap , sequential deoiling, sintering, heat treatment, processing, and surface preparation were performed like the example 10, and the radial ring which has the inside diameter shown in Table 5 was produced. Any radial ring of Table 5 is known by that the amount of preferred orientation of a radial direction is high. Moreover, as for the remanence ratio (Hk/iHc) , any radial ring had iHc of those with super- ** , and 1.1 MA/m (14.0kOe) ** 87.5%, the amount of oxygen was 0.14 – 0.16 % of the weight, the carbon content was 0.04 – 0.05 % of the weight, and nitrogen volume was 0.003 – 0.004 % of the weight.

(Example 11 of a comparison) Except having used the slurry of the example 1 of a comparison as the shaping raw material, the radial ring of Table 5 was produced like the example 11, and it

asked for the amount of preferred orientation of a radial direction.

[0034]

[Table 7]

Hap (kA/m) (kOe)	ラジアルリング 内径 (mm)	配向度 (%)	
		実施例 1 1	比較例 1 1
7 1 6 . 2 9	1 0 0	9 2 . 9	8 5 . 3
6 3 6 . 6 8	5 0	9 2 . 7	8 5 . 1
4 5 3 . 6 5 . 7	3 0	9 1 . 7	8 5 . 0
2 7 0 . 6 3 . 4	1 0	9 0 . 1	8 4 . 9

[0035] According to this invention, Table 5 shows that the high performance radial ring which does not have a bore in the former 100mm or less can be offered.

[0036]

[Effect of the Invention] When this invention was caused above as description, it was a hypoxia content, and it has a high sintered compact consistency and the manufacture approach which can obtain the rare earth sintered magnet of the high performance which raised the amount of preferred orientation compared with the former was able to be offered. Moreover, it is a hypoxia content and the R-T-B system sintered ring magnet of the high performance which has a high sintered compact consistency and has the polar anisotropy and the parallel anisotropy which raised the direction of orientation compared with the former was able to be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the important section sectional view showing other examples of the shaping equipment used for this invention.

[Drawing 2] They are a perspective view (a) explaining the logging point of the sample for evaluation of the ring magnet of this invention, and an important section sectional view (b).

[Drawing 3] It is the important section sectional view showing an example of the shaping equipment used for this invention.

[Drawing 4] It is the perspective view showing an example of the arc segment magnet of this invention which has an parallel anisotropy.

[Drawing 5] It is the perspective view showing an example of the arc segment magnet of this invention which has a radial anisotropy.

[Description of Notations]

1 Dice, 2 Bottom Punch, 3 Cavity, 4 Migration Means, 5 A supply head, 6 A slurry supply pipe, 7

A plate, 8 Sliding plate, 9 A supply head body, 10 slurry supply means, 11 Piping, 12 Control unit, 13 A tank, 15 30 A slurry feeder, 40 Arc segment magnet, 51 The dice ferromagnetism section, 52 The dice nonmagnetic section, 53 A core, 54 Top punch, 55 Bottom punch, 56 An up coil, 57 A lower coil, 58 A press frame and 59 70 A cavity, 90 Radial ring.

[Translation done.]

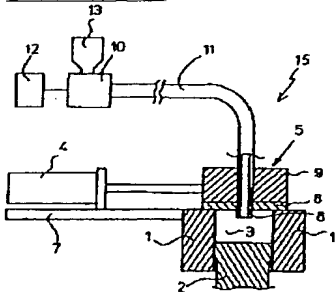
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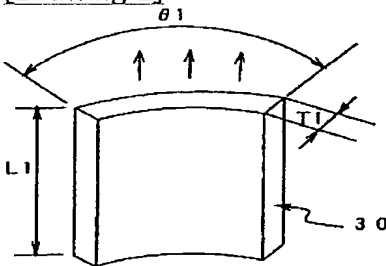
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DRAWINGS

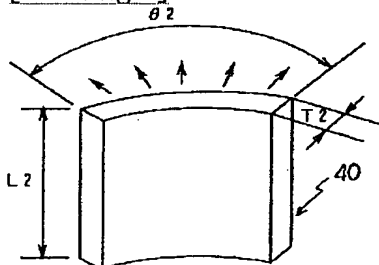
[Drawing 1]



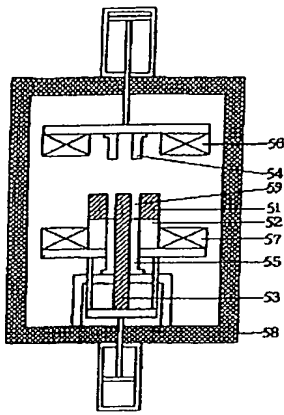
[Drawing 2]



[Drawing 3]

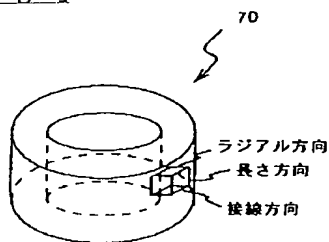


[Drawing 4]

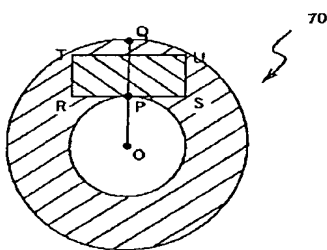


[Drawing 5]

(a)



(b)



[Translation done.]

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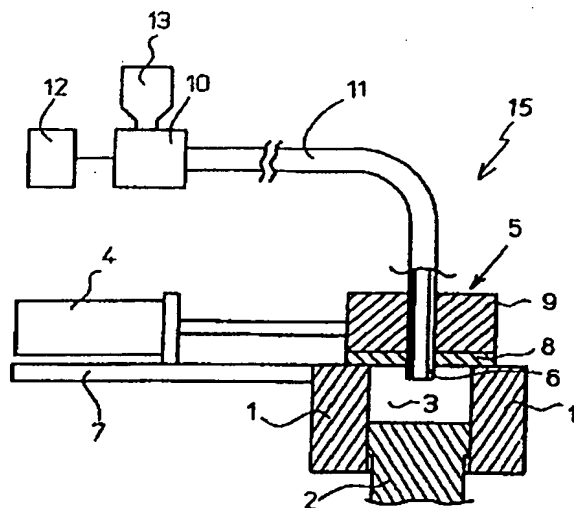
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(54)【発明の名称】 希土類焼結磁石の製造方法およびリング磁石

(57)【要約】

【課題】 低酸素含有量であり、高い焼結体密度を有し、従来に比べて配向度を高めた高性能の希土類焼結磁石を得られる製造方法を提供する。

【解決手段】 希土類焼結磁石用合金粗粉を非酸化性雰囲気中で平均粒径1~10 μ mに微粉碎し、得られた微粉を鉱油、合成油及び植物油から選択される少なくとも1種の油と、脂肪酸の1価アルコールエステル、多塩基酸の1価アルコールエステル、多価アルコールの脂肪酸エステル及びそれらの誘導体のうちから選択される少なくとも1種からなる潤滑剤とからなる非酸化性液中に回収してスラリーを作製し、次いで前記スラリーにより成形し、得られた成形体を脱油し、次いで焼結し、熱処理することを特徴とする希土類焼結磁石の製造方法。



【特許請求の範囲】

【請求項 1】 希土類焼結磁石用合金粗粉を非酸化性雰囲気中で平均粒径 $1 \sim 10 \mu\text{m}$ に微粉碎し、得られた微粉を鉱油、合成油及び植物油から選択される少なくとも 1 種の油と、脂肪酸の 1 価アルコールエステル、多塩基酸の 1 価アルコールエステル、多価アルコールの脂肪酸エステル及びそれらの誘導体のうちから選択される少なくとも 1 種からなる潤滑剤とからなる非酸化性液中に回収してスラリーを作製し、次いで前記スラリーにより成形し、得られた成形体を脱油し、次いで焼結し、熱処理することを特徴とする希土類焼結磁石の製造方法。

【請求項 2】 前記潤滑剤の添加量は、 $(R-F e-B \text{ 系合金微粉}) : (\text{潤滑剤}) = 99.99 \sim 99.5 \text{ 重量部} : 0.01 \sim 0.5 \text{ 重量部}$ となる範囲である請求項 1 に記載の希土類焼結磁石の製造方法。

【請求項 3】 前記希土類焼結磁石用合金粗粉は、 R (R は Y を含む希土類元素の少なくとも 1 種であり、 R に占める $N d$ が 50 原子% 以上である) : $28 \sim 33\%$, $B : 0.8 \sim 1.5\%$, $C o : 0.5 \sim 5\%$, $C u : 0.01 \sim 0.3\%$, $G a : 0.01 \sim 0.2\%$, $A l : 0.01 \sim 0.3\%$, $N b : 0.01 \sim 0.8\%$ 、及び残部 : $F e$ の主要成分、ならびに不可避免的不純物からなる請求項 1 または 2 に記載の希土類焼結磁石の製造方法。

【請求項 4】 重量%で、 R (R は Y を含む希土類元素の少なくとも 1 種であり、 R に占める $N d$ が 50 原子% 以上である) : $28 \sim 33\%$, $B : 0.8 \sim 1.5\%$, $C o : 0.5 \sim 5\%$, $C u : 0.01 \sim 0.3\%$ 、及び残部 : $F e$ の主要成分、ならびに不可避免的不純物を含有する $R-F e-C o-C u-B$ 系焼結磁石からなるリング磁石であって、前記リング磁石の全重量に対し不可避免的に含有される酸素量が 0.3% 以下であり、極異方性を有し、密度が 7.56 Mg/m^3 (g/cm^3) 以上であり、リング外径面での磁極間中心部表面位置で観測した (105) 面からの X 線回折ピーク強度 : $I(105)$ と (006) 面からの X 線回折ピーク強度 : $I(006)$ との比率が、 $I(105) / I(006) = 0.5 \sim 0.8$ であることを特徴とするリング磁石。

【請求項 5】 前記リング磁石は、重量%で、 $G a : 0.01 \sim 0.2\%$, $A l : 0.01 \sim 0.3\%$, $N b : 0.01 \sim 0.8\%$ を含有する請求項 4 に記載のリング磁石。

【請求項 6】 重量%で、 R (R は Y を含む希土類元素の少なくとも 1 種であり、 R に占める $N d$ が 50 原子% 以上である) : $28 \sim 33\%$, $B : 0.8 \sim 1.5\%$, $C o : 0.5 \sim 5\%$, $C u : 0.01 \sim 0.3\%$ 、及び残部 : $F e$ の主要成分、ならびに不可避免的不純物を含有する $R-F e-C o-C u-B$ 系焼結磁石からなるリング磁石であって、前記リング磁石の全重量に対し不可避免的に含有される酸素量が 0.3% 以下であり、平行異方性を有し、密度が 7.56 Mg/m^3 (g/cm^3) 以上であり、室温の保磁力 iH_c が 1.1 MA/m (14kOe) 以上であり、室温における配向方向の残留磁束密度 ($Br//$) と配向方向に垂直な長さ方向の残留

磁束密度 ($Br \perp$) とで定義する配向度 : $[(Br//)/(Br// + Br \perp)] \times 100(\%)$ が 85.5% 以上であることを特徴とするリング磁石。

【請求項 7】 前記リング磁石は、重量%で、 $G a : 0.01 \sim 0.2\%$, $A l : 0.01 \sim 0.3\%$, $N b : 0.01 \sim 0.8\%$ を含有する請求 6 に記載のリング磁石。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、低酸素含有量であり、高い焼結体密度を有し、従来に比べて配向度を高めた高性能の希土類焼結磁石を得られる製造方法に関する。又本発明は、低酸素含有量であり、高い焼結体密度を有し、従来に比べて極異方方向または平行異方性の配向度を高めた、高性能の $R-T-B$ 系焼結リング磁石に関する。

【0002】

【従来の技術】 $R-F e-B$ 系焼結磁石 (R は Y を含む希土類元素の少なくとも 1 種である) は、所定組成の $R-F e-B$ 系合金を粗粉碎し、次いで N_2 等の不活性ガス中で微粉碎し、得られた平均粒径 $1 \sim 10 \mu\text{m}$ の微粉末を磁場中成形し、次いで焼結し、熱処理することにより製造される。残留磁束密度 Br および最大エネルギー積 (BH) $_{\text{max}}$ を高めるには含有酸素量の低減が極めて重要である。このため、本出願人は前記微粉の酸化の進行を阻止する作用の顕著な鉱油や合成油を発見し、それら油中に前記微粉を回収してスラリー化し、このスラリーを成形し、次いで得られた成形体を脱油し、焼結し、熱処理することにより低酸素含有量、高密度型の高性能 $R-F e-B$ 系焼結磁石を得られる製造プロセスを提案した (特許第 2731337 号等参照)。この製造プロセスは前記微粉末及び成形体を前記油で被覆し大気と遮断することにより酸化の進行を実質的に抑えられるという特徴を有し、脱油し、焼結して得られた $R-F e-B$ 系焼結体の含有酸素量が微粉碎前の $R-F e-B$ 系合金粗粉に相当する低水準に保持される。よって $R-F e-B$ 系焼結体中の R 元素が酸化物化し、実質的に滅失して生じる有効希土類量の減少が小さく抑えられ、粒界相を形成する希土類リッチ相は健全に保持される。有効希土類量の実質的な滅失が小さい分だけ R 含有量を低く設定できるので従来に比べて余剰の R リッチ相及び希土類酸化物が低減でき、同時に強磁性相の $R_2Fe_{14}B$ 型結晶粒 (主相) の体積比率を高められるので Br , $(BH)_{\text{max}}$ が顕著に向上する。

【0003】

【発明が解決しようとする課題】 しかし最近の VCM や CD ピックアップ、家電用モータ等の磁石応用製品の小型化・軽量化のニーズは根強く、使用される希土類焼結磁石の小サイズ化および高性能化の要求は益々厳しくなっている。この要求に対し、低酸素含有量、高密度型の高性能 $R-F e-B$ 系焼結磁石を得られる前記製造プロ

セス（特許第2731337号等参照）を適用しても、本発明者らが期待したほどBr及び(BH)_{max}は高くなかった。この現象を本発明者らが詳細に調査した結果、前記スラリーの磁場配向性が十分ではなく、改良の余地を残していることがわかった。この問題に鑑み、本発明者らは既に、鉱油等の非酸化性油と非イオン性又は陰イオン性界面活性剤とを所定比率で配合してなる油中に前記微粉を回収し、得られたスラリーが良好な磁場配向性を有し、もってこのスラリーにより磁場中成形し、次いで順次脱油、焼結及び熱処理を行うことにより従来に比べてBr及び(BH)_{max}を高めた希土類焼結磁石が得られることを知見し、その製造方法（特願2000-196345号）を出願した。

【0004】本発明者らは、非イオン性又は陰イオン性界面活性剤以外で、それらと類似の効果をえられるスラリー改質剤を求めて鋭意検討した結果、スラリー改質剤として後述の潤滑剤が好適であることを発見した。このように、本発明が解決しようとする課題は、低酸素含有量であり、高い焼結体密度を有し、従来に比べて配向度を高めた高性能の希土類焼結磁石を得られる製造方法を提供することである。又本発明の課題は、低酸素含有量であり、高い焼結体密度を有し、従来に比べて極異方向または平行異方性の配向度を高めた、高性能のR-T-B系統結リング磁石を提供することである。

【0005】

【課題を解決するための手段】上記課題を解決した本発明の希土類焼結磁石の製造方法は、希土類焼結磁石用合金粗粉を非酸化性雰囲気中で平均粒径1~10 μ mに微粉砕し、得られた微粉を鉱油、合成油及び植物油から選択される少なくとも1種の油と、脂肪酸の1価アルコールエステル、多塩基酸の1価アルコールエステル、多価アルコールの脂肪酸エステル及びそれらの誘導体のうちから選択される少なくとも1種からなる潤滑剤とからなる非酸化性油中に回収してスラリーを作製し、次いで前記スラリーにより成形し、得られた成形体を脱油し、次いで焼結し、熱処理することを特徴とする。

【0006】又本発明のリング磁石は、重量%で、R

(RはYを含む希土類元素の少なくとも1種であり、Rに占めるNdが50原子%以上である)：28~33%，B：0.8~1.5%，Co：0.5~5%，Cu：0.01~0.3%、及び残部：Feの主要成分、ならびに不可避免の不純物を含有するR-Fe-Co-Cu-B系統結磁石からなるリング磁石であって、前記リング磁石の全重量に対し不可避免的に含有される酸素量が0.3%以下であり、極異方性を有し、密度が7.56 Mg/m³ (g/cm³) 以上であり、リング外径面での磁極間中心部表面位置で観測した(105)面からのX線回折ピーク強度：I(105)と(006)面からのX線回折ピーク強度：I(006)との比率が、I(105)/I(006)=0.5~0.8であることを特徴とする。前記リング磁石は、X線源にCuK α 1線(λ =0.15405nm)を用いたX線回折による(105)面からのX線回折ピーク強度：I(105)と(006)面からのX線回折ピーク強度：I(006)との比率を測定しており、I(105)/I(006)=0.5~0.8のときに、従来に比べて高いBr及び(BH)_{max}を得られる。

【0007】又本発明のリング磁石は、重量%で、R

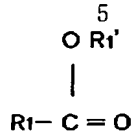
(RはYを含む希土類元素の少なくとも1種であり、Rに占めるNdが50原子%以上である)：28~33%，B：0.8~1.5%，Co：0.5~5%，Cu：0.01~0.3%、及び残部：Feの主要成分、ならびに不可避免の不純物を含有するR-Fe-Co-Cu-B系統結磁石からなるリング磁石であって、前記リング磁石の全重量に対し不可避免的に含有される酸素量が0.3%以下であり、平行異方性を有し、密度が7.56 Mg/m³ (g/cm³) 以上であり、室温の保磁力iHcが1.1MA/m(14kOe)以上であり、室温における配向方向の残留磁束密度(Br//)と配向方向に垂直な長さ方向の残留磁束密度(Br \perp)とで定義する配向度：[(Br//)/(Br//+Br \perp) \times 100(%)]が85.5%以上であることを特徴とする。

【0008】

【発明の実施の形態】本発明者らは前記スラリーの改質用潤滑剤として、炭化水素鎖(C_nH_n)からなる親油基と、化学結合の電荷分布に偏りがあって電氣的極性を有する、-OH、-COOH、-COO-、>NH₂などの極性基とで構成されている有機化学物質を検討した。鉱油、合成油あるいは植物油と前記潤滑剤とを所定重量比率で配合してなる液中にR-Fe-B系合金微粉を回収しスラリー化すると、前記潤滑剤の極性基が前記微粉粒子に吸着し、又前記潤滑剤の親油基が保護膜の役割を果たす。その吸着力の源は極性基の電氣的引力であるが、場合によってはR-Fe-B系合金微粉粒子の構成元素と反応して化学吸着することもある。このため、極性基の種類によって潤滑剤と前記微粉粒子との吸着の強さ、及び前記微粉粒子表面への単位面積当りの吸着分子数に変化し、脱油工程及びそれに続く焼結工程後の残留炭素量が顕著に変化することがわかった。また同じ極性基を有していても親油基の炭素数が多くなれば潤滑剤自体の分子量が大きくなり、揮発性が低くなって残留炭素量が増加する現象が見られた。こうして本発明者らは、第一に極性基及び親油基の種類とR-Fe-B系統結体炭素量との関係、第二に極性基及び親油基の種類と磁気特性との関係に着目し、上記課題を解決するにふさわしい潤滑剤を詳細に検討した。その結果、焼結体含有炭素量の増加が非常に小さく抑えられ、高いiHcを得られ、かつ量産に好適な高い成形体強度の得られる、[化1]の基本構造式の潤滑剤を発見した。[化1]において、R₁、R₁'は炭化水素基である。

【0009】

【化1】



【0010】本発明に好適な潤滑剤の極性基はC=O（エステル結合）に限られ、親油基の炭素数は5個以上20個以下の潤滑剤が好ましい。ここでC=O基は潤滑剤の1分子中に1個ないし2個以上含んでいてもよい。また親油基の炭化水素鎖(C_nH_m)も2個以上含んでいてもよい

(m, nは正の整数である)が、一つの親油基中の炭素数は5個以上20個以下が好ましい。親油基中の炭素量が5個未満では十分な潤滑性が得られず、磁気特性を改善することが困難である。又親油基中の炭素量が20個超では潤滑剤の分子量が過大となり沸点が上昇し、揮発性が低下して残留炭素量が0.1重量%超になり、iHcの低下を招く。あるいは潤滑が過剰になり成形体強度を低下させてしまう。親油基の炭化水素は飽和、不飽和のいずれでもよい。具体的には、本発明に用いる潤滑剤は脂肪酸の1価アルコールエステル、多塩基酸の1価アルコールエステル、多価アルコールの脂肪酸エステル及びそれらの誘導体のうちから選択される少なくとも1種である。潤滑剤の添加量は、R-Fe-B系合金微粉との比率で表わされる。配合比率は、(R-Fe-B系合金微粉)：

(潤滑剤) = 99.99~99.5重量部：0.01~0.5重量部とすることが好ましく、99.99~99.7重量部：0.01~0.3重量部がより好ましい。潤滑剤の添加量が前記範囲未満では添加効果が得られず、前記範囲を超えると成形体強度及びiHcが顕著に低下する。なお、R-Fe-B系合金微粉と潤滑剤に対する前記油の配合重量比率は特に限定されず、R-Fe-B系合金微粉表面をくまなく被覆できるとともにスラリー中にR-Fe-B系合金微粉と潤滑剤とが良好に分散し、スラリーの磁場配向性が向上するので好ましい。潤滑剤の添加時期は微粉碎前のR-Fe-B系合金粗粉に添加してもよいし、スラリー作製時点で添加してもよい。

【0011】潤滑剤として適用可能なものを下記する。例えば脂肪酸の一価アルコールエステルではカプリン酸メチル、ミリスチン酸メチル、ラウリン酸メチル、ステアリン酸メチル、オイレン酸メチル、あるいはこれらエステルのメチル基の代わりにブチル基、プロピル基、エチルヘキシル基がついているものがある。また、多塩基酸の一価アルコールエステルでは、アジピン酸ジオレイル、アジピン酸ジイソデシル、アジピン酸ジイソブチル、フタル酸ジトリデシル、フタル酸2-エチルヘキシル、フタル酸ジイソノニル、フタル酸ジデシル、フタル酸ジアルキル等がある。また、多価アルコールの脂肪酸およびその誘導体では、ソルビタントリオレエート等がある。多価アルコールの脂肪酸およびその誘導体のものよりは脂肪酸の一価アルコールエステル、または多塩基酸の一価アルコールエステルの方が若干ではあるが磁石

の配向性を向上させやすい。

【0012】本発明による希土類焼結磁石がR₂Fe₁₄B金属間化合物(RはYを含む希土類元素の少なくとも1種であり、Rに占めるNdが50原子%以上である)を主相とする場合、主要成分組成を、重量%で、R：28~33%、B：0.8~1.5%、M₁：0~0.6% (M₁はNb, Mo, W, V, Ta, Cr, Ti, Zr及びHfから選択される少なくとも1種である)、M₂：0~0.6% (M₂はAl, Ga及びCuから選択される少なくとも1種)及び残部Fe(但し、R+B+Fe+M₁+M₂=100重量%とした場合)とするのが好ましい。以下、単に%と記すのは重量%を意味するものとする。R量は28~33%が好ましい。良好な耐食性を具備するために、R量は28~32%がより好ましく、28~31%が特に好ましい。R量が28%未満では所定のiHcを得られず、33%超ではBrが著しく減少する。所定のBr及び配向度を得るために、RはNd又はNdとDy、又はNdとDyとPr及び不可避的R成分からなることが好ましい。即ち、Rに占めるNdを50原子%以上とし、Dy含有量を0.3~10%にするのが好ましい。又Rに占めるNdを90原子%以上とし、Dy含有量を0.5~8%にするのがより好ましい。Rに占めるNdが50原子%未満では資源上豊富なNdの使用が制限されて、実用性が低下する。Dy含有量が0.3%未満ではDyの含有効果が得られず、10%超ではBrが低下し所定の配向度を得られない。B量は0.8~1.5%が好ましく、0.85~1.2%がより好ましい。B量が0.8%未満では1.1MA/m (14kOe)以上のiHcを得ることが困難であり、B量が1.5%超ではBrが著しく低下する。Nb, Mo, W, V, Ta, Cr, Ti, Zr及びHfの少なくとも1種からなる高融点金属元素M₁を0.01~0.6%含有することが磁気特性を高めるために好ましい。M₁を0.01~0.6%含有することにより、焼結過程での主相結晶粒の過度の粒成長が抑制され、1.1MA/m (14kOe)以上のiHcを安定して得ることができる。しかし、M₁を0.6%超含有すると逆に主相結晶粒の正常な粒成長が阻害され、Brの低下を招く。又M₁含有量が0.01%未満では磁気特性を改良する効果が得られない。M₂元素(Al, Ga及びCu)の少なくとも1種の含有量は0.01~0.6%が好ましい。Alの含有によりiHcが向上し、耐食性が改善されるが、Al含有量が0.6%超ではBrが大きく低下し、0.01%未満ではiHc及び耐食性を高める効果が得られない。より好ましいAl含有量は0.05~0.3%である。Gaの含有によりiHcが顕著に向上するが、Ga含有量が0.6%超ではBrが大きく低下し、0.01%未満ではiHcを高める効果が得られない。より好ましいGa含有量は0.05~0.2%である。Cuの微量添加は耐食性の改善及びiHcの向上に寄与するが、Cu含有量が0.3%超ではBrが大きく低下し、0.01%未満では耐食性及びiHcを高める効果が得られない。より好ましいCu含有量は0.05~0.3%である。Coの

含有により耐食性が改善され、キュリー点が上昇し、希土類焼結磁石の耐熱性が向上するが、Co含有量が5%超では磁気特性に有害なFe-Co相が形成されあるいは $R_2(Fe, Co)_{14}$ B相が形成されて、Br及びiHcが大きく低下する。従って、Co含有量は5%以下が好ましい。一方、Co含有量が0.5%未満では耐食性及び耐熱性の向上効果が得られない。よって、Co含有量は0.5~5%が好ましい。Coを0.5~5%及びCuを0.01~0.3%含有するときに1.1MA/m (14kOe)以上の室温のiHcを得られる第2次熱処理の許容温度が広がる効果を得られ、特に好ましい。Alを0.01~0.3%含有させると保磁力向上に寄与するとともに、熱処理温度のばらつきによる保磁力の変動を低減することが可能である。またNbを0.01~0.08%含有させると焼結過程での結晶粒成長を抑制し、粗大粒の形成を抑制することができる。不可避に含有される酸素量は0.3%以下が好ましく、0.2%以下がより好ましく、0.18%以下が特に好ましい。酸素含有量を0.3%以下に低減することにより焼結体密度を略理論密度まで高めることができる。 $R_2Fe_{14}B$ 型金属間化合物を主相とするR-Fe-B系焼結磁石の場合 7.56Mg/m^3 (g/cm^3)以上の焼結体密度を安定して得られ、さらに主要成分組成、微粉碎平均粒径及び焼結温度等を適宜選択すれば 7.58Mg/m^3 (g/cm^3)以上、さらには 7.59Mg/m^3 (g/cm^3)以上のものを得ることができる。又不可避に含有される炭素量は0.10%以下が好ましく、0.07%以下がより好ましい。炭素含有量の低減により希土類炭化物の生成が抑えられ、有効希土類量が増大し、iHc及び(BH)_{max}等を高めることができる。又不可避に含有される窒素量は0.15%が好ましい。窒素量が0.15%を超えるとBrが大きく低下する。本発明の磁石には公知の表面処理被膜(Niめっき等)が被覆され、実用に供されるが、R量が28~32%でかつ窒素量が0.002~0.15%のときに良好な耐食性が付与されるのでより好ましい。又、原料合金としてCaを還元剤とする還元拡散法により作製したものを用いて本発明の磁石を作製した場合、所定のiHc及び配向度を得るために、前記磁石の全重量を100重量%としてCa含有量を0.1重量%以下(0を含まず)に抑えることが好ましく、0.03重量%以下(0を含まず)に抑えることがより好ましい。

【0013】本発明による希土類焼結磁石には SmCo_5 又は $\text{Sm}_2\text{TM}_{17}$ (TMはCo, Fe, Cu及びM'からなり、M'はZr, Hf, Ti及びVから選択される少なくとも1種である)を主相とするものが包含される。

【0014】本発明の希土類焼結磁石の製造方法における原料合金の微粉碎は不活性ガスを粉碎媒体とするジェットミル等による乾式粉碎装置または酸化を阻止できる条件に設定された湿式ボールミル等の湿式粉碎装置を用いて行うことができる。例えば、酸素濃度が0.1体積%未満、より好ましくは0.01体積%以下の不活性ガス雰囲気

気中でジェットミル微粉碎後、大気に触れないように前記不活性ガス雰囲気中から直接微粉を所定配合比率の鉱油、合成油及び植物油から選択される少なくとも1種の油と潤滑剤とからなる非酸化性液中に回収し、スラリー化する。前記微粉の平均粒径は1~10 μm が好ましく、3~6 μm がより好ましい。平均粒径が1 μm 未満では微粉の粉碎効率が大きく低下し、10 μm 超ではiHc及び配向度が大きく低下する。回収したスラリーを成形原料として、所定の成形装置により磁場中成形する。成形体の酸化による磁気特性の劣化を阻止するために、成形直後から脱油までの間前記液中で保存することが望ましい。成形体を常温から焼結温度まで急激に昇温すると成形体の内部温度が急激に上昇し、成形体に残留する油と成形体を構成する希土類元素とが反応して希土類炭化物を生成し磁気特性が劣化する。この対策として、温度100~500 $^{\circ}\text{C}$ 、真空度13.3Pa (10^{-1} Torr)以下で30分間以上加熱する脱油処理を施すことが望ましい。脱油処理により成形体に残留する油が十分に除去される。なお、脱油処理の加熱温度は100~500 $^{\circ}\text{C}$ であれば一点である必要はなく二点以上であってもよい。また13.3Pa (10^{-1} Torr)以下で室温から500 $^{\circ}\text{C}$ までの昇温速度を10 $^{\circ}\text{C}/\text{分}$ 以下、より好ましくは5 $^{\circ}\text{C}/\text{分}$ 以下とする脱油処理を施すことによっても脱油が効率よく行われる。

【0015】鉱油、合成油又は植物油として、脱油及び成形性の点から、分留点が350 $^{\circ}\text{C}$ 以下のものがよい。又室温の動粘度が10cSt以下のものがよく、5cSt以下のものがさらに好ましい。

【0016】

【実施例】以下、実施例により本発明を説明するが、それら実施例により本発明が限定されるものではない。

(実施例1) 重量%で、Nd: 23.1%, Pr: 6.4%, Dy: 1.0%, B: 0.9%, Co: 2.0%, Ga: 0.1%, Cu: 0.1%及び残部: Fe からなるR-Fe-B系合金粗粉を、酸素濃度が体積比で10ppm以下に調整した窒素ガス雰囲気中でジェットミル微粉碎し、得られた平均粒径4.0 μm の微粉をこの窒素ガス雰囲気中で大気に触れることなく鉱油(出光興産(株)製、商品名: 出光スーパーゾルPA-30)中に回収しスラリー化した。なお、平均粒径はSympatec社製レーザー回折型粒径分布測定装置(商品名: ヘロス・ロードス)により測定した。次いで得られたスラリーに所定量のオレイン酸メチルを添加し、攪拌機により混合した。スラリーの配合内訳を前記微粉: 70重量部、鉱油: 29.9重量部、オレイン酸メチル: 0.10重量部とした。このスラリーを所定の金型キャビティに注入し、配向磁場強度: 1.0MA/m (13kOe), 成形圧力: 98MPa (1.0ton/cm²)の条件で横磁場の圧縮成形を行い、15mm×25mm×10mmの直方体状の成形体を得た。また、配向方向は10mm辺方向とした。この成形体の室温強度を3点曲げ試験により測定した。なお、成形体の15mm×25mmの面が上下面になるように

曲げ試験機の治具にセットし、10mmの辺に平行に加圧し3点曲げ強度を測定した。結果を表1に示す。また同様に成形した別の成形体を真空度約66.5Pa (5×10^{-1} Torr), 200℃の条件で3時間加熱して脱油し、次いで同雰囲気中で1050℃まで昇温し、次いで1050℃で2時間保持して焼結し、その後室温まで冷却した。得られた焼結体をアルゴン雰囲気中で900℃で2時間加熱し、次いで室温まで急冷する第1次熱処理を行い、続いてアルゴン雰囲気中で480℃で1時間加熱し、次いで室温まで冷却する第2次熱処理を行い、約10mm角のR-F e-B系焼結磁石を得た。得られた焼結磁石を7mm角に加工し、磁気特性測定用試料とした。次に、室温(20℃)において11.9MA/m (150kOe)のパルス磁場を前記試料の異方性付与方向に沿って印加し、磁気特性を測定した。磁気特性は11.9MA/mのパルス磁場を印加したときの磁化の強さの最大値($4\pi I_{ms}$)を求め、配向度を($Br/4\pi I_{ms}$)で定義し、評価した。結果を表1に示す。又得られた焼結磁石の含有炭素量の分析値を表1に示す。

(実施例2~4)オレイン酸メチルの代わりにステアリン酸メチル、アジピン酸ジイソデシル、ステアリン酸2-エチルヘキシルを各々添加した以外は、実施例1と同様に各3種のスラリーを作製した。以降このスラリーを用いた以外は実施例1と同様に各R-F e-B系焼結磁石を作製し評価した。結果を表1に示す。

(比較例1)オレイン酸メチルを添加せずに、実施例1のR-F e-B系微粉と鉱油とからなるスラリーを作製し、以降このスラリーを用いた以外は実施例1と同様にR-F e-B系焼結磁石を作製し評価した。結果を表1に示す。

(比較例2)オレイン酸メチルに替えて、実施例1のスラリーにオレイルアルコールを0.1重量部添加した以外は実施例1と同様の手順でR-F e-B系焼結磁石を作製し評価した。結果を表1に示す。

(比較例3)オレイン酸メチルに替えて、実施例1のスラリーにオレイルアミンを0.1重量部添加した以外は実

施例1と同様の手順でR-F e-B系焼結磁石を作製し評価した。結果を表1に示す。

(比較例4)オレイン酸メチルに替えて、実施例1のスラリーに酢酸メチルを0.1重量部添加した以外は実施例1と同様の手順でR-F e-B系焼結磁石を作製し評価した。結果を表1に示す。

(比較例5)オレイン酸メチルに替えて、実施例1のスラリーにベヘニン酸メチルを0.1重量部添加した以外は実施例1と同様の手順でR-F e-B系焼結磁石を作製し評価した。結果を表1に示す。

【0017】実施例1の成形体強度は比較例1(潤滑剤無添加)に比べてやや低い工業生産上なら問題を発生しないレベルであることが実証された。実施例1のオレイン酸メチル、比較例2のオレイルアルコール、比較例3のオレイルアミンは各々親油基が同一(炭素数17個)であり、極性基だけが異なる(順に-COO-, -OH, >NH₂)。実施例1及び比較例2, 3から明らかなように成形体強度は潤滑剤の極性基の種類に依存することがわかる。又磁気特性は、実施例1及び比較例2, 3ではいずれも配向度($Br/4\pi I_{ms}$)は同程度であるが、実施例1に比べて比較例2, 3のiHcが低下している。比較例1を基準にすると、添加した潤滑剤の残留により焼結体炭素量が増加し、iHcが低下する程度が異なることから焼結体炭素量も極性基の種類に依存していると判断される。又、比較例4, 5は潤滑剤の極性基を-COO-とし、親油基中の炭化水素鎖の炭素数を変えたものである。比較例4の結果から、炭化水素鎖が短い場合には配向度($Br/4\pi I_{ms}$)の改善が認められないので、前記微粉間の潤滑性向上には寄与していないと判断される。一方、比較例5から、炭化水素鎖が長い場合には配向度($Br/4\pi I_{ms}$)がみられるものの、焼結体炭素量が増加してしまいiHcの低下が大きいことがわかる。

【0018】

【表1】

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	潤滑剤	親油基中の炭素数(個)	Br/4 π I ₀₀₀ (%)	(BH) _{max} (kJ/m ³) (MG0e)	iHc(MA/m) (kOe)	焼結体炭素量(wt%)	成形体強度(MPa)
実施例1	オレイン酸メチル	17	96.5	395 49.4	1.23 15.4	0.067	0.81
実施例2	ステアリン酸メチル	17	96.2	391 49.1	1.23 15.4	0.067	0.81
実施例3	アジピン酸ジイソデシル	20	96.7	394 49.5	1.23 15.5	0.067	0.79
実施例4	ステアリン酸2-エチルヘキシル	25	96.4	392 49.2	1.22 15.3	0.068	0.79
比較例1	無添加	—	95.1	377 47.4	1.23 15.5	0.065	1.34
比較例2	オレイルアルコール	17	96.3	390 49.0	1.17 14.7	0.088	0.34
比較例3	オレイルアミン	17	96.0	389 48.9	1.15 14.4	0.089	0.37
比較例4	酢酸メチル	1	95.2	379 47.6	1.23 15.5	0.066	—
比較例5	ヘヘン酸メチル	22	96.8	395 49.6	1.14 14.3	0.093	—

【0019】以下に極異方性を有する、R-T-B系統結リング磁石を作製し、評価した実施例を説明する。

(実施例5) 重量%で、主要成分組成がNd: 23.1%, Pr: 6.4%, Dy: 1.0%, B: 1.05%, Ga: 0.08%, Nb: 0.2%, Al: 0.05%, Cu: 0.13%, Co: 2.0%及び残部FeからなるR-Fe-B系原料合金粗粉(320メッシュ以下)を酸素濃度が1ppm未満(体積比)の窒素雰囲気中でジェットミル粉碎し、得られた平均粒径3.8 μ mの微粉を用いた以外は実施例1と同様にしてスラリーを作製した。得られたスラリーを、図1に示す成形機のキャビティ59に充填後、成形圧力: 78.4MPa(0.8ton/cm²)及び100Vのパルス磁場で極異方となるよう磁場中成形し、成形体を得た。成形体を真空度が約66.5Pa(5 $\times 10^{-1}$ Torr)、200℃の条件で1時間加熱し脱油後、続いて約4.0 $\times 10^{-3}$ Pa(3 $\times 10^{-5}$ Torr)、1060℃の条件で2時間焼結後室温まで冷却し焼結体を得た。次に、アルゴン雰囲気中で900℃で1時間加熱後550℃まで冷却し、次いで550℃で2時間加熱後さらに室温まで冷却する熱処理を行った。次に所定寸法に加工後、電着により平均膜厚12 μ mのエポキシ樹脂膜をコーティングし、外径48mm、内径30mm及び高さ11mmの8極の極異方性を有する極異方リングを得た。次に上記の極異方リングの外径面での磁極間中央部が測定できるようX線回折用の試料を切り出し、その試料を理学電気(株)製のX線回折装置(RU-200BH)にセットし、2 θ - θ 走査法によりX線回折した。X線源にはCuK α 1線(λ =0.15405nm)を用い、ノイズ(バックグラウンド)は装置に内蔵されたソフトにより除去した。主な回折ピークは主相であるR₂T₁₄B型金属間化合物の、2 θ =29.08°の(004)面、38.06°の(105)面、44.34°の(006)面であ

り、(006)面からのX線回折ピーク強度: I(006)を100%として、I(004)/I(006)=0.33, I(105)/I(006)=0.63であった。結果を表2に示す。

(比較例6) 実施例5のスラリーに替えて、比較例1のスラリーにより極異方方向へ磁場中成形した以外は実施例5と同様にして比較例の極異方リングを作製した。以後は実施例5と同様に比較例6の極異方リングのX線回折を行なった。結果を表2に示す。主な回折ピークは実施例5と同様であったが、I(004)/I(006)=0.32, I(105)/I(006)=0.96であった。又前記極異方リングの酸素量は0.13重量%であり、炭素量は0.05重量%であり、窒素量は0.003重量%であった。

【0020】

【表2】

	密度 (Mg/m ³) (g/cm ³)	Bo (T) (kG)	I(105)/ I(006)
実施例5	7.59	5.80 58.0	0.63
比較例6	7.59	5.48 54.8	0.96

【0021】表4の実施例5及び比較例6の結果より、本発明によれば、極異方性を有し、密度が7.56 Mg/m³(g/cm³)以上であり、リング外径面での磁極間中心部表面位置で観測した(105)面からのX線回折ピーク強度: I(105)と(006)面からのX線回折ピーク強度: I(006)との比率が、I(105)/I(006)=0.5~0.8である極異方リングを提供できることがわかる。

【0022】以下に全体が軸垂直方向へ方向に配向した(以後、平行異方性という)、R-T-B系統結リン

グ磁石を作製し、評価した実施例を説明する。

(実施例 6) 実施例 1 と同様にしてスラリーを作製した。得られたスラリーを、図 1 に示す成形機のキャビティ 59 (ダイス 51 及び 52 の内径: 60mm、コア 53 の外径: 45mm、ダイス強磁性部 51 の長さ: 34mm、充填深さ: 34mm) に充填後、成形圧力: 78.4MPa (0.8ton/cm²) 及び軸垂直方向へ一方向に磁場強度: 約 238.7kA/m (3kOe) をかけた条件で磁場中成形し、成形体を得た。以後は実施例 5 と同様にして平行異方性を有する平行異方性リングを得た。次に、図 2 に示すように、作製した前記平行異方性リング 70 の配向方向に沿って切り出し、接線方向 5mm×長さ方向 6.5mm×径方向 2.8mm の直方体を得た。直方体の切り出し要領については図 2 (b) により説明する。平行異方性リング 70 の中心点 O から半径方向に配向方向に垂直に直線 OPQ を引く。点 P は内周面との接点であり、点 Q は外周面との接点である。次に、接点 P における接線 RPS を引き、接線 RPS の長さが接点 P を中心にして 5mm になるようにする。次に、接線 RPS に垂直に直線 RT (長さ 2.8mm) 及び直線 SU (長さ 2.8mm) を引く。次に、接線 RPS に平行に直線 TU (長さ 5mm) を引く。長方形 RSUT における RPS 方向及び TU 方向が平行異方性リング 70 の接線方向であり、RT 方向および SU 方向を平行異方性リング 70 の配向方向と定義する。又、長方形 RSUT の厚み方向が平行異方性リング 70 の長さ方向であり 6.5mm の長さに切り出した。この切り出し要領により合計 4 個の直方体を切り出す。

	密度 (Mg/m ³) (g/cm ³)	Br// (T) (kG)	iHc (MA/m) (kOe)	(BH)max (kJ/m ³) (MG0e)	(Hk/iHc) (%)	配向度 (%)
実施例 6	7.60	1.35 13.5	1.27 16.0	353.3 44.4	96.4	92.3
比較例 7	7.60	1.31 13.1	1.31 16.5	319.9 40.2	87.1	89.4

【0024】表 3 の実施例 6 及び比較例 7 の結果より、本発明によれば、密度が 7.56g/cm³ 以上、配向方向における Br// が 1.25T (12.5kG) 以上、iHc が 1.1MA/m (14.0kOe) 以上、(BH)max が 282.6kJ/m³ (35.5MG0e) 以上、(Hk/iHc) が 87.5% 以上、及び配向方向の配向度が 85.5% 以上という、従来にない高い磁気特性を有する平行異方性リングを提供できることがわかる。

【0025】以下に他の実施例として平行異方性を有する、R-T-B 系焼結アークセグメント磁石を作製し、評価した実施例を説明する。

(実施例 7) 実施例 1 で作製したスラリーを図 3 のスラリー供給装置 15 の原料タンク 13 に充填した。次に、スラリー供給管 6 をシリンダー (図示省略) で下降させ、アークセグメント形状のキャビティ 3 の底面近傍位置 (下パンチ 2 の上面近傍位置) で停止させた。次に、ポンプ 10 を作動させて原料タンク 13 からスラリーを配管 11 を通してスラリー供給管 6 からキャビティ 3 に吐出しながらスラリー供給管 6 をシリンダー (図示省略) でキャビティ 3 の上端部位置まで上昇し、キャビティ 3 に所定量の

* した後、それらの各方向を一致させて貼りあわせた直方体を得た。この直方体により下記の磁気特性を測定した。なお、測定対象の平行異方性リングから前記寸法の直方体が切り出せない場合は、寸法が異なる以外は前記の切り出し要領に従い複数の直方体を切り出した後、それらの各方向を一致させて貼りあわせて寸法を調整すればよい。前記直方体の室温 (20℃) における配向方向の残留磁束密度 (Br//)、保磁力 iHc、最大エネルギー積 (BH)max 及び角形比 (Hk/iHc) を測定した。Hk は $4\pi I$ (磁化の強さ) - H (磁界の強さ) 曲線の第 2 象限において、0.9Br に相当する H の値であり、Hk を iHc で除した角形比 (Hk/iHc) は $4\pi I - H$ 減磁曲線の矩形性を示している。次に、前記直方体の室温 (20℃) における長さ方向の残留磁束密度 (Br⊥) を測定後、 $[(Br//)/(Br// + Br⊥) \times 100(\%)]$ により定義する平行異方性リングの配向度を求めた。又平行異方性リングの密度を測定した。それらの測定結果を表 3 に示す。又前記平行異方性リングの酸素量は 0.13 重量% であり、炭素量は 0.05 重量% であり、窒素量は 0.003 重量% であった。

(比較例 7) 実施例 5 のスラリーに替えて、比較例 1 のスラリーにより配向方向へ磁場中成形した以外は実施例 5 と同様にして比較例の平行異方性リングを作製し、評価した。結果を表 3 に示す。

【0023】

【表 3】

スラリーを充填した。次いでスラリー供給管 6 をシリンダー (図示省略) で上昇させてキャビティ 3 から引き抜いた後、供給ヘッド 9 をシリンダー 4 により左方向に移動し、次いで水平方向に 1.0MA/m (13kOe) の配向磁場を印加しながら上パンチ (図示省略) 及び下パンチ 2 により 98MPa (1ton/cm²) の圧力を加えて横磁場圧縮成形を行い、アークセグメント成形体を得た。以降は実施例 1 と同様にして成形体を脱油後、焼結し、熱処理した。次いで得られた焼結磁石素材表面の焼結肌が無くなるまで加工し、次いで平均膜厚 15μm のエポキシ樹脂膜をコーティングしてなる。図 4 に示す厚み $T_1 = 2.8\text{mm}$ 、長さ $L_1 = 80.0\text{mm}$ 、中心角 $\theta_1 = 45^\circ$ の薄肉、長尺形状の R-F e-B 系焼結アークセグメント磁石 30 を得た。加工前の前記素材の L_1 方向の反りは 1mm 未満であり小さく、異方性付与方向の配向度 (Br/ $4\pi I$ max) が良好であった。アークセグメント焼結磁石 30 の異方性は ↑ 方向 (紙面にほぼ垂直方向) に付与されている。前記アークセグメント磁石 30 から試料を切り出し、磁気異方性付与方向の磁気特性を室温 (20℃) で測定した結果、配向度

($Br/4\pi I_{max}$) = 96.8%、 $iH_c = 1.24 \text{ MA/m}$ (15.6 kOe) 及び $(BH)_{max} = 394.8 \text{ kJ/m}^3$ (49.6 MGOe) という高い値が得られた。又、密度は 7.60 Mg/m^3 (g/cm^3) であり、酸素量は 0.14 重量%、炭素量は 0.05 重量% 及び窒素量は 0.02 重量% であった。又、試料を理学電気(株)製の X 線回折装置 (RU-200BH) にセットし、 $2\theta - \theta$ 走査法により X 線回折 ($\text{Cu K}\alpha 1$ 線; $\lambda = 0.15405 \text{ nm}$ を使用) した結果、主な回折ピークは主相である R_2T_{14} B 型金属間化合物の、 $2\theta = 29.08^\circ$ の (004) 面、 38.06° の (105) 面、及び 44.34° の (006) 面であり、(006) 面からの X 線回折ピーク強度: $I(006)$ を 100% として、 $I(105)/I(006) = 0.66$ であった。

【0026】(実施例 8) キャビティ 3 の厚み及びスラリーの充填量を変えた以外は実施例 7 と同様にして、表 2 の長さ L_1 、厚み T_1 及び θ_1 の寸法を有する薄肉、長尺形状の焼結アークセグメント磁石を作製した。これ*

	L_1 (mm)	T_1 (mm)	θ_1 ($^\circ$)
実施例 8	72	1.0	55
		2.1	
		4.0	

【0028】以下にラジアル異方性を有する、R-T-B 系焼結アークセグメント磁石を作製し、評価した実施例を説明する。

(実施例 9) ラジアル異方性を有するアークセグメント焼結磁石用成形体の内径寸法及びラジアル配向磁場強度 (Hap) を変化させて、最終的に長さ $L_2 = 65 \text{ mm}$ 、厚み $T_2 = 2.5 \text{ mm}$ 、 $\theta_2 = 40^\circ$ 及び表 3 の内径を有する図 5 の焼結アークセグメント磁石 40 を作製し、内径と Hap 及びラジアル方向の配向度 (%) との関係を調査した。調査結果を表 3 に示す。なお、このアークセグメント焼結磁石の製造は、成形条件及び成形体寸法を変えた以外は実施例 7 と同様にして順次脱油、焼結、熱処理、加工及び表面処理を行った。表 3 よりラジアル方向の高い配向度を有することがわかる。又、表 3 のアークセグメント磁石はいずれも角形比 (H_k/iH_c) が 87.5% 超であり、 iH_c は 1.1 MA/m (14 kOe) 超であり、酸素量は 0.13~0.14 重量% であり、炭素量は 0.05~0.06 重量% であり、窒素量は 0.003~0.004 重量% であった。

(比較例 9) 比較例 1 のスラリーを成形原料とした以外は実施例 9 と同様の形状を有する焼結アークセグメント磁石用成形体の成形を試みたが、成形体亀裂が発生し、焼結アークセグメント磁石を作製することができなかった。

【0029】

【表 5】

*らの磁石は、磁気異方性付与方向の配向度 ($Br/4\pi I_{max}$) = 96.4~96.7%、 $iH_c = 1.23 \sim 1.25 \text{ MA/m}$ (15.4~15.7 kOe)、 $(BH)_{max} = 393.2 \sim 395.6 \text{ kJ/m}^3$ (49.4~49.7 MGOe) という高い磁気特性を有し、密度は 7.60 Mg/m^3 (g/cm^3) であり、酸素量は 0.13~0.14 重量%、炭素量は 0.06 重量% 及び窒素量は 0.02~0.03 重量% であった。又、実施例 7 の場合と同様にして X 線回折した結果、 $I(105)/I(006) = 0.67 \sim 0.68$ であった。

(比較例 8) 比較例 1 のスラリーを成形原料とした以外は実施例 7 と同様に横磁場成形法を適用し、 $T = 1.0 \sim 4.0 \text{ mm}$ の R-F e-B 系焼結アークセグメント磁石用成形体の成形を試みたが、成形体に亀裂が発生し、亀裂の無い健全な成形体を得られなかった。

【0027】

【表 4】

アークセグメント 内径 (mm)	Hap (kA/m) (kOe)	配向度 (%)
100	708.3 8.9	92.6
50	612.8 7.7	92.2
30	461.6 5.8	91.9
10	310.4 3.9	91.7

【0030】次に、ラジアルリングの実施例について説明する。

(実施例 10) 重量%で、主要成分組成が Nd : 21.4%、Pr : 6.0%、Dy : 3.1%、B : 1.05%、Ga : 0.08%、Nb : 0.2%、Al : 0.05%、Cu : 0.13%、Co : 2.0% 及び残部 Fe からなる R-F e-B 系原料合金粗粉 (320 Mesh) を酸素濃度が 1 ppm 未満 (体積比) のアルゴン雰囲気中でジェットミル粉碎し、得られた平均粒径 $3.8 \mu\text{m}$ の微粉を用いた以外は実施例 1 と同様にしてスラリーを作製した。得られたスラリーを、図 1 に示す成形機のキャビティ 59 (ダイス 51 及び 52 の内径: 60 mm、コア 53 の外径: 45 mm、ダイス強磁性部 51 の長さ: 34 mm、充填深さ: 34 mm) に充填後、成形圧力: 78.4 MPa (0.8 ton/cm^2) 及びラジアル方向の配向磁場強度: 約 238.7 kA/m (3 kOe) の条件でラジアル磁場中成形し、成形体を得た。成形体を真空度が約 66.5 Pa ($5 \times 10^{-1} \text{ Torr}$)、 200°C の条件で 1 時間加熱し脱油後、続いて約 $4.0 \times 10^{-3} \text{ Pa}$ ($3 \times 10^{-5} \text{ Torr}$)、 1060°C の条件で 2 時間焼結後室温まで冷却し焼結体を得た。次に、アルゴン雰囲気中

で900℃で1時間加熱後550℃まで冷却し、次いで550℃で2時間加熱後さらに室温まで冷却する熱処理を行った。次に所定寸法に加工後、電着により平均膜厚12μmのエポキシ樹脂膜をコーティングし、外径48mm、内径39mm及び高さ11mmのラジアル異方性を有するラジアルリングを得た。次に、図2に示すように、作製した前記ラジアルリング70の任意の位置から接線方向5mm×長さ方向6.5mm×ラジアル方向2.8mmの直方体を切り出した。直方体の切り出し要領について図2(b)により説明する。ラジアルリング70の中心点Oから半径方向に直線OPQを引く。点Pは内周面との接点であり、点Qは外周面との接点である。次に、接点Pにおける接線RPSを引き、接線RPSの長さが接点Pを中心にして5mmになるようにする。次に、接線RPSに垂直に直線RT(長さ2.8mm)及び直線SU(長さ2.8mm)を引く。次に、接線RPSに平行に直線TU(長さ5mm)を引く。長方形RSUTにおけるRPS方向及びTU方向がラジアルリング70の接線方向であり、RT方向およびSU方向をラジアルリング70のラジアル方向と定義する。又、長方形RSUTの厚み方向がラジアルリング70の長さ方向であり6.5mmの長さになり切り出した。この切り出し要領により合計4個の直方体を切り出した後、それらの各方向を一致させて貼りあわせた直方体を得た。この直方体により下記の磁気特性を測定した。なお、測定対*

* 象のラジアルリングから前記寸法の直方体が切り出せない場合は、寸法が異なる以外は前記の切り出し要領に従い複数の直方体を切り出した後、それらの各方向を一致させて貼りあわせて寸法を調整すればよい。前記直方体の室温(20℃)におけるラジアル方向の残留磁束密度(Br//)、保磁力iHc、最大エネルギー積(BH)max及び角形比(Hk/iHc)を測定した。Hkは4πI(磁化の強さ)－H(磁界の強さ)曲線の第2象限において、0.9Brに相当するHの値であり、HkをiHcで除した角形比(Hk/iHc)は4πI－H減磁曲線の矩形性を示している。次に、前記直方体の室温(20℃)における長さ方向の残留磁束密度(Br⊥)を測定後、[(Br//)/(Br//+Br⊥)×100(%)]により定義するラジアルリングの配向度を求めた。又ラジアルリングの密度を測定した。それらの測定結果を表4に示す。又前記ラジアルリングの酸素量は0.13重量%であり、炭素量は0.05重量%であり、窒素量は0.003重量%であった。

(比較例10) 実施例10のスラリーに替えて、比較例1のスラリーによりラジアル磁場中成形した以外は実施例10と同様にして比較例のラジアルリングを作製し、評価した。結果を表4に示す。

【0031】

【表6】

	密度 (Mg/m ³) (g/cm ³)	Br// (T) (kG)	iHc (MA/m) (kOe)	(BH)max (kJ/m ³) (MGoe)	(Hk/iHc) (%)	配向度 (%)
実施例 10	7.61	1.30 13.0	1.43 18.0	318.4 40.0	96.4	89.9
比較例 10	7.61	1.23 12.3	1.43 18.0	281.0 35.3	87.1	85.2

【0032】表4の実施例10及び比較例10の結果より、本発明によれば、密度が7.56g/cm³以上、ラジアル方向におけるBr//が1.25T(12.5kG)以上、iHcが1.1MA/m(14.0kOe)以上、(BH)maxが282.6kJ/m³(35.5MGoe)以上、(Hk/iHc)が87.5%以上、及びラジアル方向の配向度が85.5%以上という、従来にない高い磁気特性を有するラジアルリングを提供できることがわかる。

【0033】(実施例11) 図1の成形機のダイス51,52及びコア53等の寸法を変化させてラジアル異方性を有する成形体リングの内径寸法を変化させ、ラジアル配向磁場強度(Hap)を変えたときのHap、最終的に得られたラジアルリングの内径及びラジアル方向の配向度(%)の関係を調査した。Hapは表5に示すようにラジアル異方性を有する成形体リングすなわちラジアルリングの内径が小さくなるほど低下する。ラジアルリングの内径が100mmのときのHapは磁場発生用電源及びコイルの発熱等に

より716.2kA/m(9kOe)が上限であった。前記成形体リングの内径、外径(外径=内径+(8~20mm))及びHapを変えたラジアル磁場成形条件とした以外は実施例10と同様にして順次脱油、焼結、熱処理、加工及び表面処理を行い、表5に示す内径寸法を有するラジアルリングを作製した。表5のいずれのラジアルリングもラジアル方向の配向度が高いことがわかる。又、いずれのラジアルリングも角形比(Hk/iHc)は87.5%超であり、1.1MA/m(14.0kOe)超のiHcを有し、酸素量は0.14~0.16重量%であり、炭素量は0.04~0.05重量%であり、窒素量は0.003~0.004重量%であった。

(比較例11) 比較例1のスラリーを成形原料とした以外は実施例11と同様にして表5のラジアルリングを作製し、ラジアル方向の配向度を求めた。

【0034】

【表7】

Hap (kA/m) (kOe)	ラジアルリング 内径 (mm)	配向度 (%)	
		実施例 1 1	比較例 1 1
716.2 9	100	92.9	85.3
636.6 8	50	92.7	85.1
453.6 5.7	30	91.7	85.0
270.6 3.4	10	90.1	84.9

【0035】表5より、本発明によれば、内径が100mm以下の従来にない高性能ラジアルリングを提供できることがわかる。

【0036】

【発明の効果】以上記述の通り、本発明によれば、低酸素含有量であり、高い焼結体密度を有し、従来に比べて配向度を高めた高性能の希土類焼結磁石を得られる製造方法を提供することができた。又、低酸素含有量であり、高い焼結体密度を有し、従来に比べて配向方向を高めた、極異方性および平行異方性を有する高性能のR- 20 T-B系焼結リング磁石を提供することができた。

【図面の簡単な説明】

【図1】本発明に用いる成形装置の他の例を示す要部断面図である。

【図2】本発明のリング磁石の評価用試料の切り出し要領を説明する斜視図 (a)、要部断面図 (b) である。*

* 【図3】本発明に用いる成形装置の一例を示す要部断面図である。

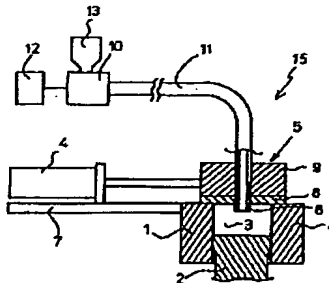
【図4】平行異方性を有する本発明のアーカセグメント磁石の一例を示す斜視図である。

【図5】ラジアル異方性を有する本発明のアーカセグメント磁石の一例を示す斜視図である。

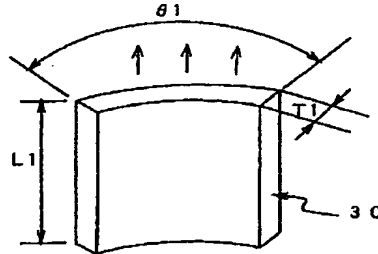
【符号の説明】

1 ダイス、2 下パンチ、3 キャビティ、4 移動手段、5 供給ヘッド、6 スラリー供給管、7 プレート、8 摺動板、9 供給ヘッド本体、10 スラリー供給手段、11 配管、12 制御装置、13 タンク、15 スラリー供給装置、30、40 アークセグメント磁石、51 ダイス強磁性部、52 ダイス非磁性部、53 コア、54 上パンチ、55 下パンチ、56 上部コイル、57 下部コイル、58 プレスフレーム、59 キャビティ、70, 90 ラジアルリング。

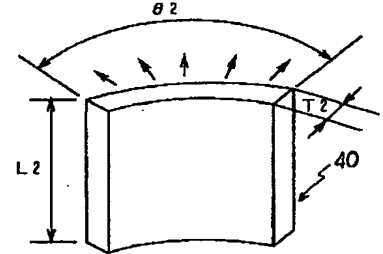
【図1】



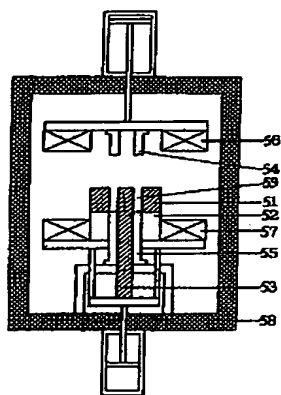
【図2】



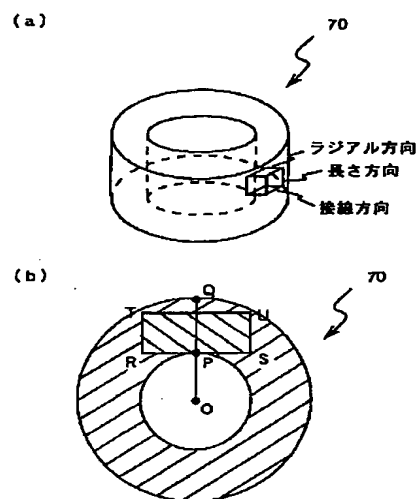
【図3】



【図4】



【図5】



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